Volume 30 No. 7 July, 1960

JOURNAL OF GENERAL CHEMISTRY of the USSR

ЖУРНАЛ ОБЩЕЙ ХИМИИ
(ZHURNAL OBSHCHEI KHIMII)

TRANSLATED FROM RUSSIAN

CONSULTANTS BUREAU

Volume 30, No. 7

July, 1960

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

(ZHURNAL OBSHCHEI KHIMII)

A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:
Vol. 19 No. 1 January 1949

	U. S. and Canada	*Foreign*
Annual Subscription	*$120.00*	*$125.00*
Annual subscription for libraries of nonprofit academic institutions	*50.00*	*55.00*
Single issue	*15.00*	*15.00*

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JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 30, Number 7 July, 1960

CONTENTS

	PAGE	RUSS. PAGE
Heats of Solution of Copper Perchlorate Hexahydrate in Water and in Aqueous Solutions of Perchloric Acid. S. A. Shchukarev, G. M. Orlova, and Z. U. Borisova	2073	2097
The System W–WS_2. S. A. Shchukarev, M. P. Morozova, and Kh. Damen	2077	2102
The Oxidizing Potential of Permanganate. I. P. Alekseeva, V. M. Pesotskaya, and B. V. Ptitsyn	2080	2104
A Study of the Thermal Stability and the Activity as Polymerization Initiators of Diacyl Peroxides of Cinnamic and Hydrocinnamic Acids. I. V. Sukmanskaya and A. I. Yurzhenko	2084	2108
The System Acetic Anhydride–Sulfuric Acid. I. Atomic Concentration, Viscosity, and Refractive Index of the System. T. V. Mal'kova	2088	2113
The System Acetic Anhydride–Sulfuric Acid. II. Synthesis of Sulfoacetic Acid and Volumetric Investigation of an "Artificial System." T. V. Mal'kova	2095	2120
Thermal Analysis of the Ternary System Acetamide–Acetic Acid–Phenylacetic Acid. V. F. Chesnokov and I. M. Bokhovkin	2099	2124
Heats of Mixing Dioxane with Chloroform and o-Toluidine. O. A. Osipov, M. A. Panina, and E. S. Yagubyan	2102	2127
Investigation of the Liquid-Vapor Phase Equilibria in the Systems Formed by $TiCl_4$ with Mono- and Trichloroacetyl Chlorides. G. V. Seryakov, S. A. Vaks, and L. S. Sidorina	2105	2130
Transalkylation Reactions in a Series of Elements of the Third and Fourth Groups (Al, B, Zn, Mg). L. I. Zakharkin and O. Yu. Okhlobystin	2109	2134
Reaction of Triphenylaluminum with Titanium Halides in Fluorobenzene of Deuterobenzene Solution. E. V. Mitrofanova, A. N. Artemov, and G. G. Petukhov	2114	2138
Aromatic Hydrocarbons. XV. Pinacols in the Diene Synthesis. V. R. Skvarchenko, Ling Wêeng-lien, and R. Ya. Levina	2117	2141
Synthesis of Hydrocarbons. LXXV. New Synthesis of 1,1,3,3-Tetraalkylcyclohexanes. R. Ya. Levina, V. K. Daukshas, and T. P. Surikova	2121	2145
Synthesis of Branched C_{12}–C_{16} Acids in the $C_nH_{2n+1}COOH$ Series. G. I. Nikishin, Yu. N. Ogibin, and A. D. Petrov	2124	2148
Study of the Alkaline Oxidation of Isopropylbenzene. II. Alkaline Protection of the Oxidation Process. V. A. Simanov and M. S. Nemtsov	2130	2153
Preparation of Allylic Type Bromide $C_7H_{13}Br$ and its Condensation by the Grignard–Wurtz Reaction. E. B. Sokolova, M. P. Shebanova, and A. P. Mrnkova	2137	2161
Identification of Alkylbenzenes. II. Analysis of Binary Mixtures of Acylamino Derivatives of 2-Phenylbutane and 3-Phenylpentane. T. E. Zalesskaya and L. E. Zhuravleva	2141	2164
Concerning the Catalytic Transformations of Ketones Isomerization of α, α-Methylethylbutyrophenone. T. E. Zalesskaya	2144	2166

CONTENTS (continued)

	PAGE	RUSS. PAGE
Esters of Phosphoric Acids with Mercury-Containing Radicals. M. S. Malinovskii, D. G. Yurko, and V. B. Tul'chinskii	2148	2170
Study of the Chemical Structure of Rubbers SKN-26 and SKN-40 by the Method of Ozonolysis. A. I. Yakubchik and A. I. Spasskova	2150	2172
Study of the Chemical Structure of the Spongy Polymer of Isoprene. A. I. Spasskova and D. I. Rabinovich	2155	2176
The Synthesis of Amides and Their Hydrochlorides from Nitriles. A. E. Kulikova, E. N. Zil'berman, and N. A. Sazanova	2159	2180
Some New Derivatives of Thiourea. Furoyl- and Benzoylthiourea. I. G. Gakh and Z. N. Nazarova	2163	2183
Chemistry of 2,1,3-Thiadiazole. XI. Chlorination and Bromination of 1',2'-Naphtho-2,1,3-Thiadiazole. V. G. Pesin, A. M. Khaletskii, and L. A. Kaukhova	2167	2187
Alkylation of Phenol by Molecular Compounds of Alcohols with Boron Fluoride. I. A. Romadan and G. T. Stipniek	2173	2193
Aralkylation of Phenol by Styrene and α-Methylstyrene. S. V. Zavgorodnyii, B. A. Zaitsev, and D. P. El'chinov	2178	2196
Investigations on Furans. VI. β-Chloroethylamines of the Furan Series. K. Yu. Novitskii, Yu. K. Yur'ev, Yu. A. Afanas'eva, I. G. Bolesov, and A. F. Oleinik	2181	2199
Investigations on Furans. VII. 2,5-Bis(Chloromethyl) Furan in the Synthesis of 2,5-Bis(Alkoxymethyl)- and 2,5-Bis(Alkylmercaptomethyl) Furans. K. Yu. Novitskii, V. P. Volkov, P. V. Kostetskii, and Yu. K. Yur'ev	2185	2203
The Chemistry of Selenophene. XXVII. Composition of the Product of Nitration of Selenophene. Yu. K. Yur'ev, E. L. Zaitseva, and G. G. Rozantsev	2189	2207
The Chemistry of Selenophene. XXVIII. Reactions of 4-Nitro- and 5-Nitro-Acetoselenophenes. Yu. K. Yur'ev, E. L. Zaitseva, and A. N. Nikiforova	2192	2209
4-Methylene-2,2,5,5-Tetramethyl-3-Furanidone. I. K. Korobitsyna, Yin Ch'en-lieh, and Yu. K. Yur'ev	2197	2214
Organophosphorus Insecticides. Derivatives of β-Dicarbonyl Compounds. M. I. Kabachnik, P. A. Rossiiskaya, M. P. Shabanova, D. M. Paikin, L. F. Efimova, and N. M. Gamper	2201	2218
Tris(Triorganosilyl) Phosphates. N. F. Orlov and M. G. Voronkov	2206	2223
Investigations of Hydroxy Derivatives of Phenanthrene. I. 1-Nitroso-2-Phenanthrol and its Bisulfite Compound. S. V. Bogdanov and L. S. Shibryaeva	2212	2229
Double Aryldiazonium Chlorides of Columbium and Tantalum. V. M. Cherkasov and I. F. Vladimirtsev	2217	2235
Investigations of Conjugated Systems. CXX. Addition of Alkyllithiums to Vinylisopropenylacetylene. A. A. Petrov, V. A. Kormer, and T. V. Yakovleva	2221	2238
Investigations of Conjugated Systems. CXXI. Addition of Alkyllithiums to Trialkylvinylethynylsilanes. A. A. Petrov, V. A. Kormer, and M. D. Stadnichuk	2226	2243
Investigations on Conjugated Systems. CXXII. Dipole Moments and Reactivities of Vinylacetylenic Ketones and Amines. A. A. Petrov, K. S. Mingaleva, I. A. Maretina, and V. D. Nemirovskii	2230	2248
Synthesis of Racemic Stereoisomeric α-Alkylparaconic Acids. N. A. Preobrazhenskii, M. E. Maurit, G. I. Bazilevskaya, G. V. Smirnova, M. M. El'manovich, A. I. Valakhanovich, and É. Persiyanova	2233	2250
Synthesis of Optically Active α-Alkyl-γ-Butyrolactone-β-Carboxylic (α-Alkylparaconic) Acids. M. E. Maurit, R. P. Shternberg, A. M. Pakhomov, G. I. Basilevskaya, G. V. Smirnova, and N. A. Preobrazhenskii	2238	2256

CONTENTS (continued)

	PAGE	RUSS. PAGE
Synthesis of the Ethyl Ester of 4, 6, 9, 11, 14-Pentaketopentadecanoic Acid and the Ethyl Ester of 4, 6, 9, 11, 14, 16, 19-Heptaketoeicosanoic Acid. N. V. Zotchik, R. P. Evstigneeva, and N. A. Preobrazhenskii.	2241	2259
Claisen Condensation of Esters of β-Methyllevulinic Acid. R. P. Evstigneeva, V. A. Glybina, E. V. Okart, and N. A. Preobrazhenskii	2243	2261
Investigations of Amines and Ammonium Compounds XII. Synthesis of Some Amines. A. T. Babayan, G. T. Martirosyan, N. G. Vartanyan, and M. G. Indzhikyan.	2245	2263
Investigations in the Field of Organic-Oxide Chemistry XVII. Interaction of Primary-Secondary Acetylenic Oxides with Methylamin. V. M. Al'bitskaya, E. M. Blyakhman, and A. A. Petrov	2250	2267
Synthesis of 2, 6-Dimethyl-Δ^1-Tetrahydrobenzaldehyde Acetals. I. N. Nazarov, R. I. Kruglikova, and S. Ya. Mel'nik	2252	2269
Synthesis of Acyl-2-Chlorocyclohexenes-2 and Ethylene Ketals of 2-Acylcyclohexanones. New Synthesis of Phenanthrenes. N. K. Kochetkov, É. E. Nifant'ev, and V. N. Shibaev.	2257	2275
Condensation of Aldehydes and Ketones VI. Conversion from Phenyl- and Furyltricyclohexanolones to 9-Phenyl- and Furylhydroacridines. M. N. Tilichenko and V. G. Kharchenko	2264	2283
Reactions of Hydrazine Derivatives XXIX. Cyanoethylation of Pyrazolones. A. N. Kost, S. I. Suminov, R. S. Sagitullin, and V. V. Ershov.	2267	2286
The Reactions of Ditertiary Butyl Peroxides with Mercurous and Mercuric Acetates with Benzoates of Mercuric Oxide, and with Metallic Mercury. Yu. A. Ol'dekop and M. M. Azanovskaya.	2272	2291
Substituted Pyridines. 2, 5-Dimethyl-4-[p(o)-Tolyl]-Pyridines and their Conversions. N. S. Prostakov, N. N. Mikheeva, A. V. Igumnova, and G. I. Zimina	2275	2294
Synthesis of 2-Tert-Butylbutadiene-1, 3. A. A. Korotkov, L. F. Roguleva, and V. A. Tsitokhtsev.	2278	2298
Amines with Gangliolytic Activity III. Branched-Chain Secondary Diamines. N. K. Kochetkov, A. Ya. Khorlin, and L. A. Vorotnikova.	2283	2303
Studies in the Field of Quinones XXXIII. Condensation of Arylnaphthoquinones with Sodium Enolates of Acetoacetic and Malonic Esters and their Analogs. A. N. Grinev, A. S. Mezentsev, and A. P. Terent'ev	2286	2306
Researches on Quinones XXXIV. Condensation of p-Quinones with Imines of Acetylacetone. A. N. Grinev, V. L. Florent'ev, V. I. Shvedov, and A. P. Terent'ev	2291	2311
Studies in the Field of the Quinones. XXXV. The Bromination of the "Acid Complex" of p-Benzoquinone by the Method of Chelintsev. A. N. Grinev, V. L. Florent'ev, and A. P. Terent'ev	2296	2316
Organic Insectofungicides LV. The Synthesis of Some Alkyl Aryl Thiophosphoric Acid Hydrazides. A. G. Zen'kevich, P. G. Zaks, Ya. A. Mandel'baum, and N. N. Mel'nikov.	2298	2317
Organic Insectofungicides LVI. The Reaction of Bis(Dialkoxythiophosphonium)-Disulfides with Triaryl- and Diarylphosphites. N. N. Mel'nikov, K. D. Shvetsova-Shilovskaya, and M. Ya. Kagan.	2300	2319
Some Derivatives of 5-Halofuran Carboxylic Acids. Z. N. Nazarova and I. G. Gakh	2304	2322

CONTENTS (continued)

	PAGE	RUSS. PAGE
Syntheses and Rearrangements in the Thiazoline Imine Series I. The Condensations of Chloroacetone and α-Chlorocyclohexanone with Symmetrical Diaryl- and Arylacylthioureas. K. M. Murav'eva and M. N. Shchukina	2308	2327
Syntheses and Rearrangements in the Thiazoline Imine Series II. The Condensation of ω-Bromoacetophenone with N-Phenyl-N'-Acylthioureas. K. M. Murav'eva and M. N. Shchukina	2315	2334
Syntheses and Rearrangements in the Thiazoline Imine Series III. The Rearrangement of 2-Imino-3-Phenyl-4-Thiazolines into 2-Phenylaminothiazoles. K. M. Murav'eva and M. N. Shchukina	2320	2340
Syntheses and Rearrangements in the Thiazolinimine Series IV. Action of Acetylating Agents on 2-Acylimino-4-Hydroxythiazolidines. K. M. Murav'eva and M. N. Shchukina	2324	2344
New Methods of Synthesis of Esters of Phosphonic and Thiophosphonic Acids XXXIV. Addition of Dialkylthiophosphorous Acids and Acid Esters of Ethyl- and Phenyl-Phosphinic Acids to Unsaturated Hydrocarbons. A. N. Pudovik and I. V. Konovalova	2328	2348
Studies in the Field of Heterocyclic Chemistry XXXIII. The Synthesis of Quinazolone Compounds on the Basis of Anthranilic Acid Arylamides. P. A. Petyunin and Yu. V. Kozhevnikov	2333	2352
Some Properties of Enolacetates V. Vinylation of Carbonyl Compounds. I. V. Machinskaya, V. A. Barkhash, and A. T. Prudchenko	2338	2357
Some Properties of Enolacetates VI. Bromo-substituted Enolacetates in the Wurtz-Grignard Reaction. I. V. Machinskaya, V. A. Barkhash, and A. T. Prudchenko	2343	2363
The Reaction of Tetrafluoroethylene with Boron Trichloride. Kh. R. Raver, A. B. Bruker, and L. Z. Soborovskii	2347	2366
Cyclization of Substituted Phenylhydrazones of the Ethyl Ester of α-Keto-γ-Diethylaminobutyric acid, Using the Method of E. Fischer. A. Ya. Berlin and V. N. Zaitseva	2349	2368
Fluorination of a Complex Acetonitrile with Boron Trifluoride. M. A. Énglin, S. P. Makarov, S. S. Dubov, L. A. Krasnousov, and A. Ya. Yakubovich	2353	2371
Fluorination of Silver and Potassium Cyanates. A. Ya. Yakubovich, M. A. Énglin, and S. P. Makarov	2356	2374
Synthesis of Some 2-Hydroxy-4-Alkoxybenzophenones. N. A. Larin, E. N. Matveeva, and V. S. Smirnova	2359	2377
Sulfonation of β-Diketones XI. Derivatives of Dimedone-2-Sulfonic Acid. É. Gudrinietse, G. Vanag, and L. Mazhal'ke	2361	2379
Radical Reactions of Percarbonates I. Thermal Decomposition of Dibenzyl and Dicyclohexyl Peroxydicarbonates in Benzene and Isopropanol. G. A. Razuvaev and L. M. Terman	2368	2387
Methods of Synthesizing 1, n-Diethoxymethylchloromethylsiloxanes and Substitutions of the Chlorine in the α-Chloromethyl Group. K. A. Andrianov and L. M. Volkova	2374	2393
Reactions of Bis(Phenylaminomethyl) Tetramethyldisiloxane with Acids. K. A. Andrianov and L. M. Volkova	2378	2397
Catalytic Condensation of Aromatic Ketones with Schiff's Bases from p-Aminobenzoic Esters and Aromatic Aldehydes. N. S. Kozlov and V. D. Pak	2381	2400

CONTENTS (continued)

	PAGE	RUSS. PAGE
Autooxidation of p-Ethyl-Sec-Butylbenzene. S. V. Zavgorodnii and V.G. Shalganova	2384	2402
Reactions of Nitrogen Oxides with Polyfluorinated Ethylenes. Preparation and Reduction of Polyfluorinated Nitroso Compounds. V. A. Ginsburg, N. F. Privezentseva, N. P. Rodionova, S. S. Dubov, S. P. Makarov, and A. Ya. Yakubovich	2388	2406
Reactions of Halogens, Nitric Oxide, and Polyfluorinated Ethylenes in Ultraviolet Light. Preparation and Thermal Decomposition of Polyfluorinated Aliphatic Nitroso Compounds. V. A. Ginsburg, N. F. Privezentseva, V. A. Shpanskii, N. P. Rodionova, S. S. Dubov, A. M. Kokhlova, S. P. Makarov, and A. Ya. Yakubovich	2391	2409
Polarographic Investigation of Glyoxylic Acid. V. D. Bezuglyi, V. N. Dmitrieva, T. S. Tarasyuk, and N. A. Izmailov	2396	2415
Internal Complex Compounds as Contact Insecticides. A. P. Terent'ev, E. A. Viktorova, B. M. Esel'son, A. N. Kost, and V. V. Ershov	2402	2422
Reaction of 8-Caffeinealdehyde with Dialkylphosphorous Acids. B. P. Lugovkin	2407	2427
LETTERS TO THE EDITOR		
Order of Addition of Water and Alcohols to Vinylacetylenes. A. A. Petrov and B. S. Kupin	2410	2430
Polymerization of Substituted Divinyl Ketones with the Formation of Rings. S. G. Matsoyan and M. G. Avetyan	2412	2431
N-Di-(Chloroethyl)-Amides of Amino Carboxylic Acids and their Peptides I. Method of Preparing N-Di-(Chloroethyl)-Amide of Glycine and Related Compounds. T. S. Safonova and S.I. Sergievskaya	2414	2432
Similarity in Chemical Structure and Biological Activity of Ribonuclease and Increpan. S. V. Andreev, R. P. Evstigneeva, A. M. Mirzabekov, N. P., Speranskaya, and N. A. Preobrazhenskii	2416	2433
Synthesis of N-(D-β-Tetraacetylglucopyranosyl)-Indole. N. N. Suvorov and M. N. Preobrazhenskaya	2417	2434
Cyclopropylmesitylene and p-Cyclopropylcumene. R. Ya. Levina, V. N. Kostin, P. A. Gembitskii, S. M. Shostakovskii, and E. G. Treshchova	2419	2435
DISCUSSION		
Physicochemical Investigation of the Binary System Hydrazine-Acetic Acid. V. I. Semishin	2421	2436
Synthesis of 2, 3, 6-Trimethylocta-2, 7-Dien-6-ol(3-Methyllinalool). F. N. Stepanov.	2422	2437

HEATS OF SOLUTION OF COPPER PERCHLORATE HEXAHYDRATE IN WATER AND IN AQUEOUS SOLUTIONS OF PERCHLORIC ACID

S. A. Shchukarev, G. M. Orlova, and Z. U. Borisova
Leningrad State University
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2097-2102, July, 1960
Original article submitted July 6, 1959

In the present work, which was undertaken as part of a plan for the systematic study of the heats of solution of the perchlorates of metals of group IV of D. I. Mendeleev's periodic system [1], we investigated copper perchlorate hexahydrate. The work was carried out over a wide range of concentrations, from very dilute up to saturated solutions, in order to obtain information that has been lacking up to this time on the thermodynamic properties of solutions with a high content of the salt. Furthermore, special attention was given to the influence exerted on the heat of solution by an excess of perchloric acid.

EXPERIMENTAL

The investigation of the heats of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in water and in aqueous solutions of perchloric acid was carried out with the aid of a microcalorimeter working on the dilatometric principle [1] at 25 ± 0.01°C. The capillaries of the calorimeter were standardized with respect to the heat of solution of KCl in water, which is 4194 ± 3 cal at 25°C. The average values obtained for one scale division were 0.0503 ± 0.0006 cal with a relative error of 1.2% for the first capillary, and 0.1903 ± 0.0004 cal with a relative error of 0.3% for the second capillary. The copper perchlorate hexahydrate was prepared by dissolving copper acetate (pure) in 40% perchloric acid (analytically pure). The compound obtained was recrystallized three times. The copper perchlorate hexahydrate was isolated in the form of fine, blue, hygroscopic crystals that deliquesced in the air, and the drying, storage, and all of the work with the compound were therefore carried out in a manipulator over concentrated sulfuric acid.

The compound was analyzed for Cu^{++} and ClO_4^- content. The copper content was determined by titration with Trilon B with murexide as the indicator. The accuracy of the analysis was 0.05%. The determination of the ClO_4^- was made by reduction of the ClO_4^- ion to Cl^- and further determination of the Cl^- ion by Mohr's method. The error of the analysis was 0.02-0.03%.

For the determination of the heats of solution we used a sample for which the analytical data for the cation and anion coincided with the theoretical values (within the limits of error of the analysis), i. e., the compound corresponded to the composition $Cu(ClO_4)_2 \cdot 6H_2O$.

The experimental values found for the heats of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in water are given in Table 1 and Fig. 1.

The heats of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in aqueous solutions of perchloric acid were determined for dilutions of 1:50 , 1:100, 1:200, and 1:500. In the experiments 66.6% perchloric acid was used, which was first distilled in vacuum. Aqueous solutions of perchloric acid of the following concentrations were prepared: 0.1, 0.5, 1.0, 2.0, 5.0, and 10.0 N.

A weighed sample of the copper perchlorate hexahydrate was dissolved in such a quantity of perchloric acid of the given concentration that a solution of the salt of the necessary concentration was obtained.

TABLE 1. Heats of Solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in Water

Dilution	ΔH_{av} (Cal/mole)	Dilution	ΔH_{av} (Cal/mole)
1 : 2000	4.70 ± 0.20	1 : 100	5.05 ± 0.05
1 : 1000	4.70 ± 0.10	1 : 50	5.04 ± 0.05
1 : 700	4.70 ± 0.10	1 : 25	5.08 ± 0.05
1 : 500	4.73 ± 0.05	1 : 15	5.41 ± 0.05
1 : 400	4.76 ± 0.05	1 : 10	5.91 ± 0.05
1 : 300	4.93 ± 0.05	1 : 8	6.27 ± 0.05
1 : 200	5.00 ± 0.05	1 : 6	6.81 ± 0.05

Note. For dilutions 1:2000-1:100 the results were obtained in the microcalorimeter with capillary No. 1: for dilutions 1:50-1:6 they were obtained with capillary No. 2. The heats of solution for dilutions greater than 1:25 were determined by direct solution of a weighed sample of the salt in the given quantity of water; for dilutions less than 1:25 the copper perchlorate hexahydrate was dissolved not in water, but in a solution of a certain concentration, the heat of formation of which was known.

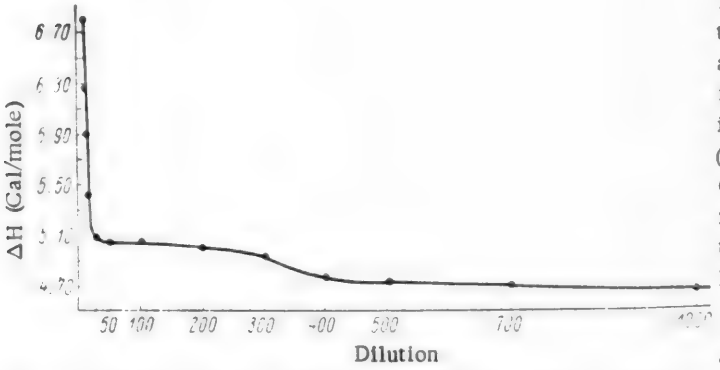

Fig. 1. Relation of heat of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in water to dilution.

The value of the heats of solution of copper perchlorate hexahydrate in perchloric acid solutions obtained experimentally are given in Table 2 and in Figs. 2-4.

It follows from the data in Table 1 and Fig. 1 that with a decrease in dilution the endothermal effect of solution of copper perchlorate hexahydrate increases from 4.70 to 6.81 Cal/mole. The heat of solution for a dilution of 1:700, which is 4.70 Cal/mole, can be taken as the first integral of the heat of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in water and is in agreement with the value indicated in the literature [2].

ΔH_{av} for the solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in water varies with dilution in the same way as in the case of the hexahydrates of the perchlorates of Mg^{++}, Zn^{++}, Co^{++}, and Ni^{++}, i. e., at dilutions of 1:25-1:30 a distinct change takes place in the course of the relationship ΔH_{av} vs. dilution. Thus, for $Cu(ClO_4)_2 \cdot 6H_2O$ in going from a dilution of 1:25 to 1:15 the endothermal effect of solution increases by 0.3 Cal/mole, while with a decrease in dilution by almost 40 times, from 1:1000 to 1:25, the endothermal effect increases by an amount of the same order (by 0.4 Cal/mole). The heat of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ differs considerably in its magnitude from those of the hexahydrates of the perchlorates of Mg^{++}, Zn^{++}, Co^{++}, and Ni^{++} [1].

It is known that $Cu(ClO_4)_2 \cdot 6H_2O$ has a different structure for its crystal lattice (monoclinic syngony) than the hexahydrates of the perchlorates of the cations mentioned above (hexagonal syngony) [3].

It is interesting to compare the magnitude of the endothermal effect of solution ($\Delta H^X = \Delta H'' - \Delta H'$) for $Cu(ClO_4)_2 \cdot 6H_2O$ and $Me(ClO_4)_2 \cdot 6H_2O$ (Me = Zn^{++}, Co^{++}, Ni^{++}) in going from maximum dilutions ($\Delta H'$) to dilutions close to saturated solutions ($\Delta H''$). The value of ΔH^X should to some extent characterize the different degree of reaction of the given cations with water (Table 3).

The hexahydrates of the perchlorates can be arranged according to the magnitude of ΔH^X in the following series: $Zn^{++} > Cu^{++} > Co^{++} > Ni^{++}$.

The heat of solution of copper perchlorate hexahexahydrate in 0.1-10.0 N solutions of perchloric acid, like that in water, is endothermal and the heats of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in water and in 0.1 N $HClO_4$ solution have the same values (within the limits of error of the experiments) for each of the dilutions mentioned (Curve 2, Fig. 2). Our attention is attracted by the fact that the heat effect of the solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in 0.5 N $HClO_4$ solution is less than in water and in 0.1 N $HClO_4$ solution, and with a further increase in concentration of the acid to 2.0 N the heat effect does not change (Curve 1, Fig. 2).

The values given on page 2076 can be accepted for the heats of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in 0.5-2.0 N solutions of perchloric acid.

TABLE 2. Heats of Solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in Aqueous Solutions of $HClO_4$

Dilution	ΔH (Cal/mole)						
	concentration of $HClO_4$ (N)						
	0.0	0.1	0.5	1.0	2.0	5.0	10.0
1 : 50	5.04 ± 0.05	5.00 ± 0.05	4.80 ± 0.05	4.82 ± 0.05	4.87 ± 0.05	6.80 ± 0.10	
1 : 100	5.05 ± 0.05	5.02 ± 0.05	4.88 ± 0.05	4.83 ± 0.05	4.85 ± 0.05	6.76 ± 0.05	10.76 ± 0.03
1 : 200	5.00 ± 0.05	4.94 ± 0.05	4.74 ± 0.05	4.74 ± 0.05	4.76 ± 0.05	6.68 ± 0.05	10.54 ± 0.05
1 : 500	4.73 ± 0.05	4.79 ± 0.05	4.73 ± 0.05	4.73 ± 0.05	4.66 ± 0.05	6.21 ± 0.05	10.16 ± 0.05

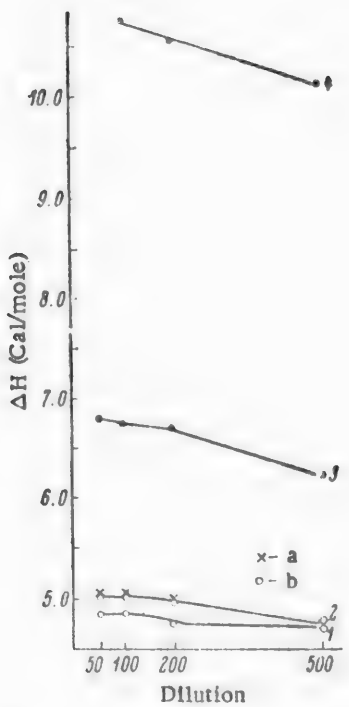

Fig. 2. Relationship of heat of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in perchloric acid to dilution. 1) For 0.5-2.0 N $HClO_4$; 2) in water (a), in 0.1 N $HClO_4$ (b); 3) in 5.0 N $HClO_4$; 4) in 10.0 N $HClO_4$.

TABLE 3. Comparison of the Magnitudes of the Endothermal Effect of Solution of the Hexahydrates of the Perchlorates of Different Cations

Meaning of Me in salt $Me(ClO_4)_2 \cdot 6H_2O$	$\Delta H''_{av}$ (Cal/mole)	$\Delta H'_{av}$ (Cal/mole)	ΔH^x
Zn	3.75	1.40	2.35
Co	3.80	1.93	1.87
Ni	3.64	2.00	1.64
Cu	6.81	4.70	2.11

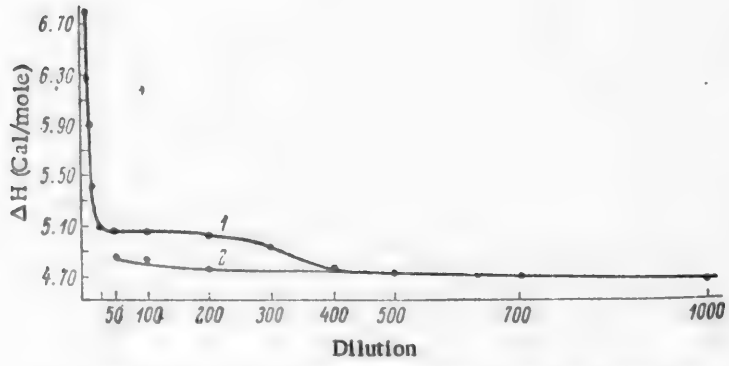

Fig. 3. Relationship of the heat of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in water and 0.5-2.0 N perchloric acid to dilution. 1) In water; 2) in perchloric acid.

Dilution	ΔH_{av} (Cal/mole)
1:50	4.83±0.05
1:100	4.85±0.05
1:200	4.74±0.05

As in the case of the solution of the hexahydrate in water, when it is dissolved in aqueous 0.5-2.0 N solutions of perchloric acid in the dilution range 1:50-1:100 the heat of solution does not change and it decreases on going to a dilution of 1:200. The decrease in endothermal effect of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in the indicated solutions of $HClO_4$ in comparison with solution in water is slight and averages 0.23 Cal/mole for dilutions of 1:50, 1:100, and 1:200.

In Fig. 3 the relationship of ΔH (Cal/mole) vs. dilution is given for solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in water and in 0.5-2.0 N $HClO_4$ solutions. In the region of dilutions 1:50-1:400 the curve for the acid solutions is smoother and is located lower than in the absence of the acid.

It is interesting to note that at a dilution of 1:500 there was practically no lowering of the endothermal effect of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in 0.1-2.0 N solutions of $HClO_4$ observed.

When $Cu(ClO_4)_2 \cdot 6H_2O$ was dissolved in 5.0 and 10.0 N solutions of perchloric acid, a considerable increase in the endothermal effect of solution was observed (Curves 3 and 4, Fig. 2). When $Cu(ClO_4)_2 \cdot 6H_2O$ was dissolved in 10.0 N $HClO_4$ solution the endothermal effect increased almost 2 times in comparison with the effect of solution in water.

In Fig. 4 the relationship of ΔH_{av} to $HClO_4$ concentration is shown. It can be seen that the endothermal effect of solution decreases at first, remains unchanged in the region of acid concentration 0.5-2.0 N and then sharply increases for dilutions of 1:100, 1:200, and 1:500.

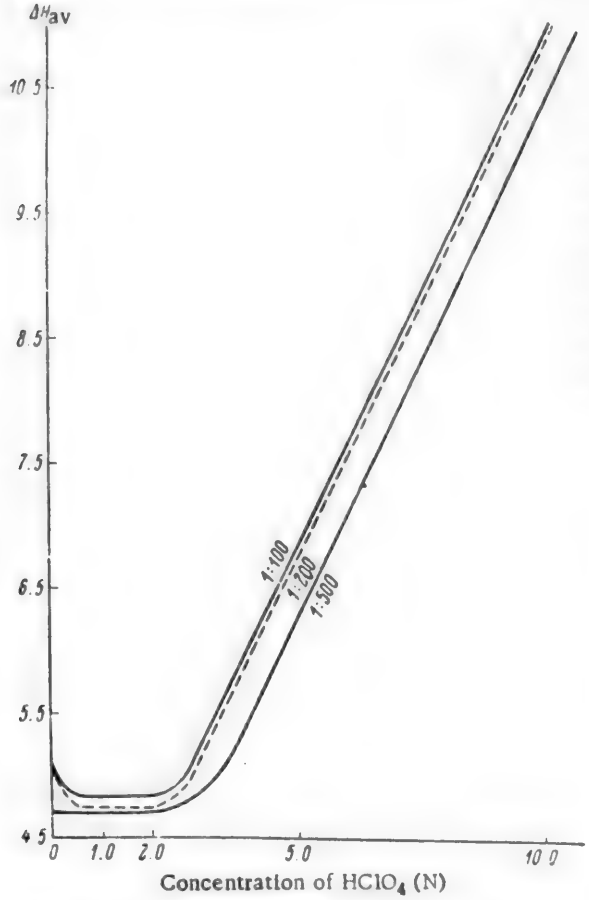

Fig. 4. Relationship of heat of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in perchloric acid to concentration of acid.

SUMMARY

1. The heats of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in water have been determined over a wide range of dilutions. It has been shown that the relationship with dilution is similar to that obtained previously for the hexahydrates of the perchlorates of Mg^{++}, Zn^{++}, Co^{++}, and Ni^{++}.

2. The heats of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in 0.1-10.0 N $HClO_4$ solutions have been determined for dilutions of 1:50, 1:100, 1:200, and 1:500. It has been shown that the heat of solution of $Cu(ClO_4)_2 \cdot 6H_2O$ depends on the concentration of the acid.

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THE SYSTEM W–WS_2

S. A. Shchukarev, M. P. Morozova, and Kh. Damen
Leningrad State University
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2102-2104,
July, 1960
Original article submitted July 8, 1959

While rather wide regions of homogeneity often exist for the sulfides of the 3ds elements, for example in the case of the sulfides of titanium [1], vanadium [2], chromium [3], iron [4], nickel [5], and cobalt [5], the question of the extent of regions of homogeneity for the sulfides of the 4d5s and the 5d6s elements has been explored comparatively little.

The formation of subcompounds also frequently is characteristic of the 3d4s elements (Co_3S_4, Co_6S_5, Co_9S_8, Ni_3S_2, subsulfides of titanium, vanadium, etc.). It still is not completely clear whether such componds of the 5d6s elements are formed.

The purpose of our investigation was to study the phase relationships in the system W–WS_2. Samples of WS_x were prepared by homogenization of mixtures of metallic tungsten powder, obtained by the reduction of WO_3 with hydrogen to constant weight at 900°, and sulfur, which had been purified by distilling 3 times in vacuum. These mixtures were placed in evacuated quartz ampoules at 800° and were roasted for 500 hours.

The tungsten content of the preparations was established by burning them to WO_3 and the sulfur was determined by difference.

Preparations having four different compositions were made: $WS_{0.91}$, $WS_{1.73}$, $WS_{1.98}$, and WS_2. The results of an x-ray study that we carried out were in complete agreement with the data obtained by Erlich [6]: over the whole range of composition W–WS_2 only lines for tungsten and the disulfide were found in the x-ray photos. Furthermore, when the composition of the preparation was changed, no change was observed in the interplanar distances in the two lattices. This indicates the absence in tungsten disulfide of an appreciable region of homogeneity extending in the direction of a lower sulfur content than that corresponding to the stoichiometric composition.

When mixtures of tungsten with sulfur in larger amounts than that necessary for the formation of WS_2 were calcined, we did not succeed in preparing homogeneous samples. Even under conditions of very slow cooling of the ampoules, the samples contained free sulfur that distilled off at a temperature of 100-150°. This obviously indicated also the absence in tungsten disulfide of a region of homogeneity extending in the direction of a higher sulfur content than that corresponding to the stoichiometric composition.

In view of the fact that the changes in a lattice parameter when the composition is changed within the limits of the region of homogeneity sometimes are very slight and may not be detected in the course of an experiment, we carried out a series of isopiestic experiments. Weighed samples of sulfides of different composition (or of sulfide and metallic tungsten powder) were taken in small quartz tubes and were placed in a quartz ampoule, which was carefully evacuated, filled with hydrogen to a pressure of 125 mm Hg and sealed. The ampoule was then kept at 600° for 200 hours. It can be seen from the data in the table that no transfer of sulfur from the sulfide of composition $WS_{1.98}$ to the metallic tungsten was observed. The same was true of the pair $WS_{1.73}$–$WS_{0.91}$.

At 600° tungsten disulfide is reduced by hydrogen and the metallic tungsten reacts with the hydrogen sulfide. Accordingly the absence of any transfer of sulfur in the experiments described clearly indicates the

absence in tungsten disulfide of a region of homogeneity extending in the direction of a lower sulfur content (in comparison with the stoichiometric composition of WS_2), and also the absence of intermediate compounds between W and WS_2.

Preparation	Time	Weight of sample	Amount of sulfur transferred (in mg)	Final composition
W	200	0.1500	0	W
$WS_{1.98}$	200	0.0859	0	$WS_{1.98}$
$WS_{0.91}$	200	0.2358	0	$WS_{0.91}$
$WS_{1.73}$	200	0.1262	0	$WS_{1.73}$

Thus the passage from chromium to tungsten is characterized by the disappearance of regions of homogeneity and of discrete compounds not corresponding to a whole-number valence condition. In the system Cr–S, according to Jellinek [7], the following compounds exist: CrS, Cr_7S_8, Cr_5S_6, and Cr_2S_3, while Haraldsen [3] found two broad regions of homogeneity. Apparently the difference in the data of the two authors is explained by the fact that they worked with preparations that were seasoned at different temperatures; the picture observed for the sulfides of the elements of the subgroup of group VI is rather typical.

Movement in the subgroups in the direction of an increase in the atomic number as a rule is accompanied by the disappearance in the compounds of perceptible regions of homogeneity (or a considerable reduction in their area). Thus, for example, vanadous oxide belongs to the group of compounds with very wide regions of homogeneity ($VO_{0.86}$–$VO_{1.27}$) [8], while niobium monoxide has a very narrow (almost imperceptible) region of homogeneity. Other examples also might be cited.

In the lattices of salt-type compounds of variable composition atoms of some element coexist in different valence states. Accordingly a number of authors consider the variable valence of a certain element to be a necessary condition for the formation of its compounds of variable composition [9, 10]. Attention is attracted by the fact that in a case where the stable valence states of a certain element differ by two or more valence units, its oxides and sulfides do not have broad regions of homogeneity.

Actually niobium does not exhibit a valence of three with respect to oxygen, the compound following NbO is NbO_2, and niobium monoxide has no observable region of homogeneity.

On the other hand, the broad region of homogeneity of vanadous oxide corresponds to the existence for vanadium of VO and V_2O_3. Tungsten exhibits only a valence of four with respect to sulfur and, as stated above, WS_2 does not have a perceptible region of homogeneity, while chromium, which exhibits "contiguous" valences of two and three with respect to sulfur, forms compounds with it that are characterized by considerable regions of homogeneity (in any case at high temperatures).

Ferrous oxide is one of the typical compounds of variable composition, but the lower oxide of the neighboring compound to iron, manganese, does not have an appreciable region of homogeneity in thermodynamic equilibrium [11]. It is possible that this fact is in conformity with the assumptions that in Mn_2O_3 and Mn_3O_4 manganese is not trivalent and di- and trivalent, respectively, but (in both compounds) di-and tetravalent.

SUMMARY

1. It has been established that in the system W–S there is one compound, WS_2, which has no perceptible region of homogeneity.

2. Some rules for the change in regions of homogeneity of oxides and sulfides in the periodic system have been discussed.

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*Original Russian pagination. See C. B. translation.

THE OXIDIZING POTENTIAL OF PERMANGANATE

I. P. Alekseeva, V. M. Pesotskaya, and B. V. Ptitsyn
Leningrad Technological Institute for the Food Industry
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2104-2108,
July, 1960
Original article submitted July 6, 1959

It is known that potassium permanganate is widely used as an oxidizing agent, but up to the present time there has not been sufficiently complete quantitative information on the oxidizing properties of permanganate. It is known that this depends to a great extent on the acidity of the solution. There are contradictory data in the literature on this question. Thus, Kolthoff [1] found that the change in the oxidizing potential of a permanganate solution per pH unit in the pH interval 0-7 is 95 mv. Rius and de Castro [2] indicated for this same pH interval a change in potential of 60 mv per pH unit. Kolthoff, Rius, and de Castro measured the potential in buffered solutions.

A study of the relationship between the potential of a permanganate solution and the pH is of interest also because from the nature of the curve for the relationship of the potential to pH it is possible to pass judgment on the reduced form present in equilibrium with the permanganate ion. In acid solution the permanganate ion may be present in equilibrium with a whole series of its reduction products, with the exception of compounds of divalent manganese, since $KMnO_4$ oxidizes Mn^{II} at any pH value and consequently the ordinarily cited equation cannot serve to characterize the oxidizing properties of permanganate. Different methods have been used for the study of these equilibria: measurement of the oxidizing potentials of several systems, isotope exchange [3-5], etc. The system $MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$ has been studied the most, but the data on the value of the normal oxidizing potential are contradictory [6, 7].

$$E = 1510 + \frac{59.1}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{++}]}$$

The nature of the acid may influence the value of the oxidizing potential. This has been shown for bichromate solution in the work of B. V. Ptitsyn and V. F. Petrov [8]. The same may occur also for permanganate.

The problem in the present investigation was, first, to clarify the quantitative relationship of the oxidizing potential of a permanganate solution to the pH of the medium; second, to determine whether the nature of the acid affects the value of the potential; and third, to attempt to characterize the equilibria existing in a permanganate solution under our conditions.

Starting Materials and Methods of Work

Twice-distilled water was used in preparing all of the solutions. The second distillation was carried out from an alkaline solution of permanganate. The potassium permanganate solution was prepared from the chemically pure salt that had been recrystallized three times. The titer of the solution was determined with oxalic acid. The solutions of acids were prepared from concentrated chemically pure acids. For the connecting bridges and intermediate cells, recrystallized KNO_3 and KCl were used.

The measurements of the oxidizing potential and the pH of the permanganate solution were made with a type LP-5 pH meter. A smooth platinum electrode was used as an indifferent electrode, and a saturated calomel electrode was used as the standard electrode for comparison. In order to avoid decomposition of the permanganate, the contact between the solution under investigation and the calomel electrode was made through an intermediate cell filled with a saturated solution of KNO_3, by means of two connecting bridges. The opening of the bridge

was in contact with the permanganate solution and was filled with KNO_3 solution and covered with glass wool. The second bridge was filled with saturated KCl solution. The pH was measured with a glass electrode. When the oxidizing potential was measured in each test, readings were taken simultaneously with two electrodes. The measurements of the potential were made at 25°.

In the course of the work it was determined that stirring had no effect on the value and the rate of establishment of the potential.

Relationship of Oxidizing Potential of Permanganate to pH in the Presence of Different Acids

The relationship of the oxidizing potential of a potassium permanganate solution to the pH was determined in solutions of perchloric, nitric, sulfuric, and acetic acids. The permanganate concentration in all the experiments was 0.01 M.

The relationship of the oxidizing potential of permanganate to the pH in solutions of the acids mentioned is shown in the figure. The values of the oxidizing potentials in all cases are given in millivolts with reference to a hydrogen electrode and are the averages of not less than 5-7 experiments with an average error of ± 4 mv.

From an inspection of the curves obtained the following facts can be seen.

1. The curves for the relationship of the oxidizing potential of a permanganate solution to the pH for perchloric and nitric acids coincide over the pH range investigated. The value of the oxidizing potential of permanganate in solutions of these acids within the indicated pH interval is a linear function of pH. The change in potential per pH unit is 84 mv.

TABLE 1.

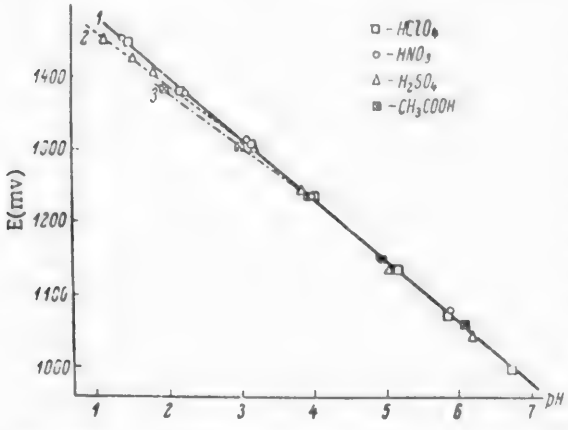
pH	1.40	2.10	3.10	4.00	5.15	5.85	6.75
E (mv)	1449	1382	1309	1236	1135	1072	998

By way of illustration, data are presented in Table 1 on the relationship of the potential of permanganate to the pH in $HClO_4$ solutions.

2. The curve for sulfuric acid coincides with the curve for $HClO_4$ and HNO_3 at pH > 3 and lies somewhat below it at pH < 3. In the interval pH 3-1 the slope of the curve is 74 mv per pH unit.

3. The curve for acetic acid diverges from the curve for $HClO_4$ and HNO_3 at pH < 4. The slope of the curve in the region pH 4-2 is 74 mv per pH unit, i. e., in this interval the curve is parallel to the curve for sulfuric acid in the region pH 3-1.

The equilibrium between the permanganate ion and the reduced forms in acid medium can be represented by different electrochemical equations, each of which should, according to the Nernst equation, be characterized by a certain value of $\Delta E/\Delta pH$ (Table 2).



Relationship of oxidizing potential of potassium permanganate to pH in the presence of different acids. 1) In $HClO_4$ solution and in HNO_3 solution; 2) in H_2SO_4 solution; 3) in CH_3COOH solution.

If we compare the experimentally obtained change in potential per pH unit with the changes in potential corresponding to the equilibria given, then it may be assumed that in $HClO_4$ and HNO_3 solutions the permanganate ion is in equilibrium mainly with manganese dioxide. Some difference between the experimentally obtained value of $\Delta E/\Delta pH$ and its theoretical value (from equation 2) possibly is associated with the fact that Mn^{IV} may be present in the solution partly in the form of $MnO^{\bullet\bullet}$ or $Mn^{\bullet\bullet\bullet\bullet}$ ions. The possibility of the existence of the latter in an acid solution of permanganate has been pointed out by Latimer and a number of authors who have studied the isotope exchange between the MnO_4' ion and its reduced forms [7]. An analysis of the curves for H_2SO_4 and CH_3COOH makes it possible to assume that in the pH region from 6 to 3 for H_2SO_4 and from 6 to 4 for CH_3COOH the permanganate is in equilibrium with the same reduced forms. In the pH regions from 3 to 1 for H_2SO_4 and from 4 to 2 for CH_3COOH the slope of the

TABLE 2. Values of $\Delta E/\Delta pH$ for Different Oxidation-Reduction Systems

Equation No.	System	$\Delta E/\Delta pH$
1	$MnO_4' + 2H^+ + 2\bar{e} \rightleftarrows MnO_3' + H_2O$	59
2	$MnO_4' + 4H^+ + 3\bar{e} \rightleftarrows MnO_2 + 2H_2O$	79
3	$MnO_4' + 8H^+ + 3\bar{e} \rightleftarrows Mn^{++} + 4H_2O$	157
4	$MnO_4' + 6H^+ + 3\bar{e} \rightleftarrows MnO^{+} + 3H_2O$	118
5	$MnO_4' + 8H^+ + 4\bar{e} \rightleftarrows Mn^{+++} + 4H_2O$	118
6	$MnO_4' + 5H^+ + 4\bar{e} \rightleftarrows Mn(OH)_3 + H_2O$	74

curves is the same ($\Delta E/\Delta pH$=74 mv). On the basis of this observation it can be assumed that the permanganate in both instances is in equilibrium with the same reduced form, namely $Mn(OH)_3$.

The formation of compounds of trivalent manganese as the form in equilibrium with the permanganate ion it seems to us may be connected with the formation of sulfate and acetate complexes when the concentration of the corresponding acids increases. In the literature there are indications that when permanganate is reduced in the presence of complex-forming agents, compounds of trivalent manganese may appear [9]. Complexes of Mn^{III} with sulfate ion are known. The existence of similar complexes of Mn^{III} with the acetate ion can be assumed with an adequate degree of likelihood.

The curve for the relationship of the oxidizing potential of permanganate to the pH begins to be determined by Equation 6 for solutions of CH_3COOH at larger pH values than for solutions of H_2SO_4. This may be associated, first, with the greater concentration of CH_3COOH than of H_2SO_4 for equal pH values, and second, perhaps, with the greater capacity of the acetate ion for complex formation. The latter factor should also elicit a relatively larger sluft in the equilibrium in the direction of the reduced form, leading to a decrease in the concentration of the permanganate ion and to a corresponding decrease in the potential, which is confirmed by comparison of the position of curves 2 and 3 in the figure. The relatively unstable complexes of Mn^{III} are decomposed by water with the formation, as a final result, of a hydrated oxide of trivalent manganese, which also is in equilibrium with the permanganate ion.

The different change in the potential per pH unit in our experiments and in references [1] and [2] can be explained by the fact that we established the necessary pH value by the addition of the appropriate acids and NaOH to the permanganate solution, but the authors mentioned carried out their measurements in buffered mixtures. In this connection Kolthoff pointed out the possibility of some reaction of the permanganate with the Clark buffer mixtures.

If we extrapolate curves 1 and 2 in the figure to pH=0 and bring the concentration of permanganate to 1 M according to Equation 2 (Table 2) for $HClO_4$ and HNO_3 and Equation 6 for H_2SO_4, then it is possible to approximately evaluate the oxidation potential of the permanganate solution under these conditions. For $HClO_4$ and HNO_3 E=1600 mv and for H_2SO_4 E=1650 mv.

SUMMARY

1. The relationship of the oxidizing potential of 0.01 M $KMnO_4$ solution in solutions of $HClO_4$, HNO_3, H_2SO_4, and CH_3COOH has been investigated.

2. It has been shown that the nature of the acid has an effect at low pH values.

3. On the basis of an analysis of the curves for the relationship of the potential of a solution of $KMnO_4$ to the pH in solutions of different acids, a hypothesis has been stated regarding the nature of the reduced forms that are present in equilibrium with the permanganate ion.

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A STUDY OF THE THERMAL STABILITY AND THE ACTIVITY AS POLYMERIZATION INITIATORS OF DIACYL PEROXIDES OF CINNAMIC AND HYDROCINNAMIC ACIDS

I. V. Sukmanskaya and A. I. Yurzhenko

L'vov Medical Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2108-2112, July, 1960
Original article submitted July 3, 1959

Because of the small energy of the −O−O− bond [1] in the molecule of peroxides under the conditions of polymerization of monomers they break down to free radicals, which initiate the polymerization process. Among the organic peroxides those that have been studied the most as initiators of polymerization are the alkyl, aryl, and alkylaryl hydroperoxides; this is to a considerable extent associated with their wide use in emulsion (latex) polymerization [2]. We find considerably less data on thermal stability and initiating activity for the diacyl peroxides [4, 5], with the exception of benzoyl peroxide [3]. Because of their oleophilic nature the diacyl peroxides may have special value as polymerization initiators in cases where the polymerization process must necessarily be carried out in a mass of the monomer, for example in pearl polymerization.

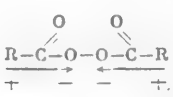
The purpose of the present investigation was the comparative study of the thermal stability and the initiating activity of diacyl peroxides of benzoyl, cinnamic, and hydrocinnamic acids. It was of interest of determine the effect of the −CH=CH− and $-CH_2-CH_2-$ groups introduced between the −O−O− group and the phenyl radical on the indicated properties of the diacyl peroxides.

An investigation of the kinetics of the thermal breakdown of the peroxides that have been mentioned in chloroform at 70 and 80° showed (Table 1) that the introduction between the phenyl radical and the peroxide group of the −CH=CH− and the $-CH_2-CH_2-$ links leads to a lowering of the stability of the peroxide and an acceleration of its dissociation. The energy of activation of the process decreased in the order benzoyl peroxide–cinnamic acid peroxide–hydrocinnamic acid peroxide, which also serves as an indication of the weakening of the −O−O−bond in the same sequence.

TABLE 1. Rate Constants and Energy of Activation of the Dissociation of Diacyl Peroxides (min^{-1}). Solvent–Chloroform

Peroxide	70° $k \cdot 10^5$	80° $k \cdot 10^5$	E, Cal
$(C_6H_5CO)_2O_2$	1.05	0.33	27.4
$(C_6H_5CH=CH-CO)_2O_2$	2.35	0.89	27.0
$(C_6H_5CH_2-CH_2CO)_2O_2$	5.67	1.77	26.8

The cause of this weakening, in our opinion, must be the weakening of the inductive effect that is dependent on the phenyl radical. Actually we should represent the diacyl peroxide as two dipoles joined together and being in a state of repulsion.



Because of this, the greater excess negative charge there is localized on the oxygen atoms of the peroxide group, the more the −O−O− bond is weakened. Because of the electrophilic nature of the phenyl group, this charge will be less in benzoyl peroxide, thus providing higher stability. With the introduction of the −CH=CH− group, and especially of the $-CH_2-CH_2-$ group, the effect of the phenyl radical is weakened, which results in a weakening of the −O−O−bond and consequently to a lowering of the stability of the peroxide.

A comparative study of the initiating activity of the peroxides under investigation was carried out with the aid of experiments on the polymerization of styrene in the presence of the indicated diacyl peroxides as initiators. It was found that with other conditions being equal the rate of polymerization of the styrene increased on going from benzoyl peroxide to the peroxide of hydrocinnamic acid (Table 2). Thus, the initiating activity of the peroxides increases in the same order in which their thermal stability decreases.

TABLE 2. Average Rate of Polymerization (v_{pol}) of Styrene (moles/liter·min) in the Presence of Diacyl Peroxides. Temperature 70°

Conc. of peroxides (moles/1000 g)	$v_{pol} \cdot 10^3$ in the Presence of		
	Benzoyl Peroxide	Peroxide of cinnamic acid	Peroxide of hydrocinnamic acid
0.05	2.416	3.35	3.558
0.025	1.666	2.20	2.256
0.0125	1.204	1.69	1.778
0.0063	0.864	1.10	1.187

To obtain comparative data on the rate of initiation of the reaction in the presence of the peroxides under investigation, we determined the molecular weights of the styrene polymers that were formed. In this way it was found that the polymers obtained with the peroxide of cinnamic acid in the majority of cases were not soluble in benzene, which fact probably was associated with the possibility of partial copolymerization of the styrene and the cinnamic acid, which has a double bond in the side chain.

TABLE 3. Comparative Data on Rate of Initiation v_{in} (moles/liter·min). Temperature 70°

Conc. of peroxides (moles/1000 g)	$v_{in} \cdot 10^5$ in the presence of	
	Benzoyl peroxide	Peroxide of hydrocinnamic acid
0.05	1.205	2.00
0.025	0.664	0.93
0.0125	0.293	0.47
0.0063	0.192	0.29

The relative value of the rate of initiation (v_{in}) was found from the relationship $v_{in} = v_{pol}/P$ where v_{pol} is the over-all rate of polymerization and P is the average degree of polymerization [6].

The data on the rate of initiation presented in Table 3 show that the peroxide of hydrocinnamic acid provides the most rapid course for the initiation reaction, and therefore it can be recommended for the synthesis of polymerized plastics as an active oleophilic initiator.

EXPERIMENTAL

The peroxide of cinnamic acid was prepared by the method of Pechmann and Vanino [7], but the concentration of hydrogen peroxide was increased to 16-20%. The peroxide was purified by reprecipitation twice by methyl alcohol from a solution in chloroform.

The peroxide of hydrocinnamic acid was prepared by a somewhat modified version of the method given in [8] for the preparation of an aliphatic diacyl peroxide: to a mixture of 10 ml of 20% hydrogen peroxide with 10 ml of 16.5% alkali solution cooled with water and ice was added dropwise, with stirring, 10 g of hydrocinnamic acid chloride. After all the acid chloride had been added, the mixture was stirred for 30-40 minutes more. The precipitate of peroxide that had separated out was filtered off and washed with ice water, and then 2-3 times with small portions of cold methyl alcohol. The yield of peroxide was 70-80%. The percent of active oxygen was determined iodometrically.

Found %: 5.38, 5.35. Calculated %: 5.37.

The starting styrene, which contained 99.9% of the monomer, was freed of inhibitor (hydroquinone) by ditilling it 3 times in vacuum after a preliminary treatment with concentrated alkali solution.

In order to study the rate of thermal breakdown of the peroxides under investigation we prepared approximately 0.065 M solutions of them in chloroform. Glass ampoules with a capacity of 15-18 ml were filled with these solutions, 7 ml being placed in each ampoule; the ampoules were sealed and placed in a water thermostat in which a constant temperature was maintained within ±0.05°. The decomposition of the peroxides was studied at 70 and 80°. At certain time intervals ampoules were taken from the thermostat, cooled quickly with ice water, and opened. Five ml of solution was taken from the ampoule and the amount of undecomposed peroxide in it was determined iodometrically.

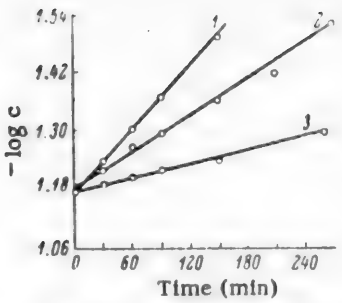


Fig. 1. Thermal breakdown of diacyl peroxides in chloroform at 70°; 1) peroxide of hydrocinnamic acid; 2) peroxide of cinnamic acid; 3) benzoyl peroxide.

To determine the specific initiating activity of the peroxides under investigation, we carried out the polymerization of styrene en masse in their presence. The styrene was polymerized in a special dilatometer vessel, which was a graduated 2-ml pipet with a glass bulb of about 20-ml capacity sealed on. A solution of the peroxide in styrene was poured into the previously weighed dilatometer; the dilatometer was reweighed, sealed, and placed in a water thermostat. The speed of the polymerization process was determined by the contraction.

The molecular weights of the polymers were determined by viscosimetry.

Comparative data on the rate of thermal decomposition of the peroxides investigated at 70° are given in Fig. 1. It can be seen that the relationship -log c vs. t, where c is the concentration of undecomposed peroxide in the solution and t is the time in minutes, has an almost linear character. This shows that under the given conditions the breakdown of the peroxides mentioned can be described closely enough by an equation of the first order. A similar picture has been noted for the breakdown of a diacyl peroxide (benzoyl peroxide) in other research also [9, 10].

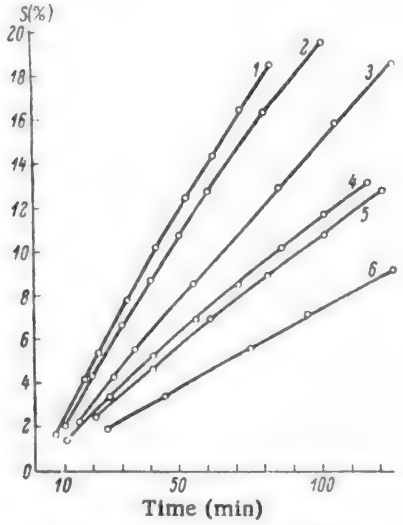


Fig. 2. Curves for the polymerization of styrene at 70°; 1, 2, 3) hydrocinnamyl, cinnamyl, and benzoyl peroxides; concentration of peroxides 0.050 mole/1000 g of styrene; 4, 5, 6) same peroxides; concentration 0.0125 mole/1000 g

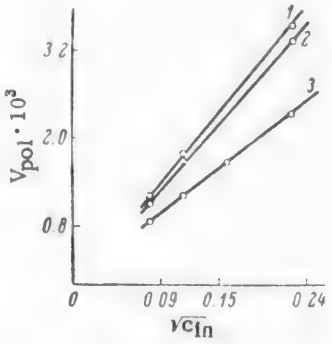


Fig. 3. Rate of polymerization of styrene in the presence of diacyl peroxides; c_{in}=concentration of peroxides; 1) peroxide of hydrocinnamic acid; 2) peroxide of cinnamic acid; 3) benzoyl peroxide.

It is necessary, however, to keep in mind that such a picture for the breakdown of benzoyl peroxide (and, obviously, similar compounds) is far from being always observed. Nosaki and Bartlett [11], who investigated the breakdown of benzoyl peroxide in detail in various solvents, showed that on the thermal breakdown of the peroxide (1) there may be superimposed its induced breakdown (2) brought about by the reaction of the radicals that are formed with the peroxide molecules, and that this situation can be represented by the following scheme:

(1)
$$\left.\begin{aligned} &C_6H_5{-}CO{-}O{-}O{-}CO{-}C_6H_5 \longrightarrow 2C_6H_5{-}CO{-}O{-}\cdot \\ &2C_6H_5{-}CO{-}O{-}\cdot \longrightarrow CO_2 + C_6H_5{-}CO{-}O{-}C_6H_5 \end{aligned}\right\}$$

(2)
$$\left.\begin{aligned} &C_6H_5{-}CO{-}O{-}\cdot + C_6H_5{-}CO{-}O{-}O{-}CO{-}C_6H_5 \longrightarrow \\ &\longrightarrow CO_2 + C_6H_5{-}CO{-}O{-}C_6H_5 + C_6H_5{-}CO{-}O{-}\cdot \end{aligned}\right\}$$

In connection with this, the kinetics of the breakdown of benzoyl peroxide can be represented by the equation

$$-\frac{dc}{dt} = k_1 c + k_2 c^x,$$

where k_1 and k_2 are the rate constants for the thermal breakdown and the induced breakdown; x is the order of the reaction of induced breakdown, the value of which is from 0.5 to 2. In the presence of various inhibitors the induced breakdown should be suppressed ($k_2 = 0$) and we have a first order equation to deal with. The data in Fig. 1 show that under the conditions of our experiments induced breakdown is practically absent. This is also indicated by the fact that the rate constant found by us for the breakdown of benzoyl peroxide (Table 1) is very close to the values of k_1 found by Swain et al. [12]. The role of the inhibitor was played by oxygen in our experiments. Induced breakdown may have been absent also because of the small starting concentrations of the peroxides in solution.

In Fig. 2 the kinetic curves for the polymerization of styrene in the presence of the diacyl peroxides under investigation are given. In the first stages of the polymerization process the curves for the extent of polymerization (S) and time (t) are straight lines. From the tangent of the angle of slope of the kinetic curves in their linear portions ($\Delta S/\Delta t$) the average rate of polymerization (v_{pol}) was found from the relationship

$$v_{pol} = \frac{\Delta (M)}{\Delta t} = \frac{\Delta S d_{\mu}}{\Delta t M_0},$$

where $d\mu$ and M_0 are the density and the molecular weight of the monomer.

Data on the rate of polymerization over a wider range of concentrations of the peroxides investigated are shown in Fig. 3. Here the rate of polymerization is given as a function of $\sqrt{c_{in}}$. This relationship is linear, as also follows from the theory of vinyl polymerization.

SUMMARY

1. The rate of thermal breakdown and the initiating activity of a number of diacyl peroxides (namely, benzoyl, cinnamyl, and hydrocinnamyl peroxides) have been studied. It has been found that the peroxides investigated can be arranged with respect to thermal stability in the series: benzoyl peroxide > peroxide of cinnamic acid > peroxide of hydrocinnamic acid, which is associated with the effect of the groups present between the peroxide oxygen and the phenyl radical.

2. The activity of the peroxides mentioned as initiators for the polymerization (in a mass of the monomer) increases in the same order as their thermal stabilities decrease, and this is confirmed by data on the total rate of polymerization in going from benzoyl peroxide to the peroxide of hydrocinnamic acid, and also by comparative data on the rate of initiation.

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THE SYSTEM ACETIC ANHYDRIDE – SULFURIC ACID

I. ATOMIC CONCENTRATION, VISCOSITY, AND REFRACTIVE INDEX OF THE SYSTEM

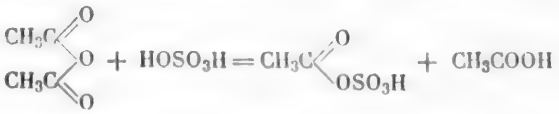
T. V. Mal'kova

Ivanovo Chemicotechnological Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2113-2120,
July, 1960
Original article submitted February 5, 1959

At the end of the last century it became known that small additions of sulfuric acid promote the acetylation of cellulose by acetic anhydride in acetic acid solution [1]. The condensations accomplished with the aid of acetic anhydride and sulfuric acid increased the interest of investigators in the system acetic anhydride–sulfuric acid. At the present time mixtures of acetic anhydride with sulfuric acid are used for the acetylation of cellulose on a commercial scale. In laboratory synthesis they are used for the acetylation of some aromatic compounds and also compounds of the aliphatic series.

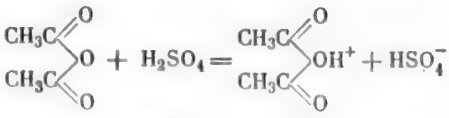
Several investigators [2-5] have assumed that acetylsulfuric acid is formed in this system.



(1)

Supporters of another point of view assume the formation in the system of addition products of sulfuric acid and acetic anhydride [6, 7].

Gillespie [7], on the basis of a measurement of the depression in the freezing point of solutions of acetic anhydride in sulfuric acid, proposed a reaction mechanism that is described by the following equations:



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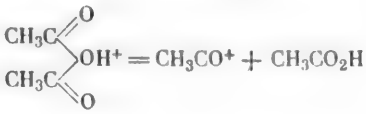

(3)

$$CH_3CO_2H + H_2SO_4 = CH_3CO_2H_2^+ + HSO_4^- \quad (4)$$

$$(CH_3CO)_2O + 2H_2SO_4 = CH_3CO^+ + CH_3CO_2H_2^+ + 2HSO_4^- \quad (5)$$

The author considered the acetyl ions completely stable in sulfuric acid solution and assumed that they are formed practically quantitatively when small amounts of acetic anhydride are dissolved in sulfuric acid .

Leisten [8] suggested another explanation of the depression in freezing point. In his opinion, there takes place in the system the extraction of water from the solvent and the addition of a proton to the acetic acid that is formed:

$$(CH_3CO)_2O + 3H_2SO_4 = 2CH_3CO_2H_2^+ + 2HSO_4^- + SO_3 \quad (6)$$

$$SO_3 + HSO_4^- = HS_2O_7^- \quad (7)$$

The proposed mechanism is in agreement with conductivity data, according to which only one hydrosulfate ion is formed per molecule of acetic anhydride in the system.

Many investigators also have observed that in the course of time more extensive changes take place in the system. These changes have been explained by the formation of sulfoacetic acid.

We believed that amplification of the physicochemical measurements of this system might lead to some clarification of the ideas of the process of reaction of acetic anhydride with sulfuric acid. In this work we confined ourselves to the study of the atomic concentration, viscosity, and refractive index.

The atomic concentration method of physicochemical analysis was proposed by I. I. Zaslavskii [10].

Separate fragmentary data on the density and viscosity of mixtures of acetic anhydride and sulfuric acid have been reported in the work of Atsuki and Ishii [11] without indications of temperature measurements. The viscosity of dilute solutions of acetic anhydride in sulfuric acid has been determined by Schwab and Kolb [12]. These data, however, are totally insufficient for the construction of viscosity diagrams and diagrams of the increase in atomic concentration in comparison with its additive values.

In our work we used acetic anhydride with b. p. 139-140° (760 mm) and sulfuric acid monohydrate (0.4-1% excess SO_3). Some excess of sulfur trioxide was permitted in order to guarantee that the sulfuric acid was free of water, small quantities of which might get into the acid from the air during the work.

For the preparation of the mixtures, a weighed quantity of acetic anhydride was placed in a three-necked 200-ml flask. The flask was provided with an anchor stirrer with a mercury seal and a thermometer. The flask was cooled externally with a mixture of ice and salt. A dropping funnel with a weighed amount of sulfuric acid was placed in the free neck and closed with a calcium chloride tube. The rate of addition of the sulfuric acid from the funnel was regulated so that the temperature of the mixture did not rise above 0°. After all the sulfuric acid had been added, stirring was continued for another 30 minutes. The dropping funnel was reweighed.

After the preparation of the mixtures, measurements of the density at 0, 25, and 40.6°, of the viscosity at 0 and 25°, and of the refractive index at 25° were carried out quickly. (The temperature that we took as 0° corresponded in fact to the range 0.05-0.15°. The temperatures of 25 and 40.6° were maintained within ±0.05°.) Repeated determinations of the properties of the mixtures directly after their preparation gave variable results. Therefore the mixtures in the pycnometer and the viscosimeters were always kept in thermostats for a strictly determined time (20 minutes), and only the first determination was used for calculations.

Then the mixtures were left in the dark at room temperature for 13 days, after which the viscosity determinations at 0, 25, and 40.6° and the density determinations at 0 and 25° were repeated. Subsequent determinations of the density at the three temperatures indicated above were made after 38 days from the time of preparation of the mixtures.

The methods of determining the density, viscosity, and refractive index, and also the calculation of the value ΔA have been indicated by us previously [13].

The viscosimeters were calibrated with respect to water, sulfuric acid, glycerol, dibutyl phthalate, and mixtures of the last with castor oil, which M. I. Arkhipov [14] has shown to be most convenient and exact.

ATOMIC CONCENTRATION

On the basis of volume measurements at 0, 25, and 40.6° at different times after the preparation of the mixtures, we calculated the deviation of the atomic concentration from the additive value (ΔA). In Fig. 1

the isotherms for ΔA obtained for the system directly after preparation are juxtaposed. They are curves with a maximum, sharply arched from the abscissa axis. The maximum is somewhat extended and its height increases with an increase in temperature from 10 at 0° to 10.6 gram-atoms/liter at 40.6°. The position of the maxima corresponds to 54.9 mole % (41 vol. %) of sulfuric acid, i.e., it does not correspond to a rational composition of the components.

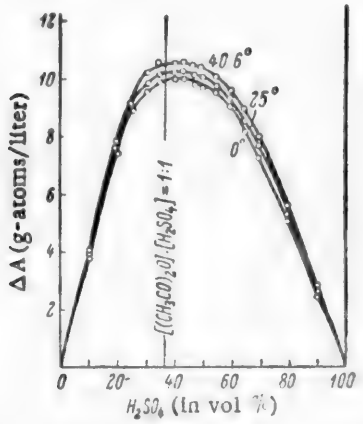

Fig. 1. Deviation of atomic concentration of the system $(CH_3CO)_2O$–H_2SO_4 from the additive value (ΔA) directly after preparation of mixtures.

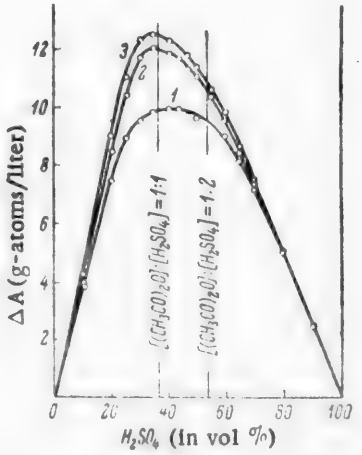

Fig. 2. Deviation of atomic concentration of the system $(CH_3CO)_2O$–H_2SO_4 from the additive value (ΔA): Temperature 0°; 1) directly after mixing; 2) after 13 days; 3) after 38 days.

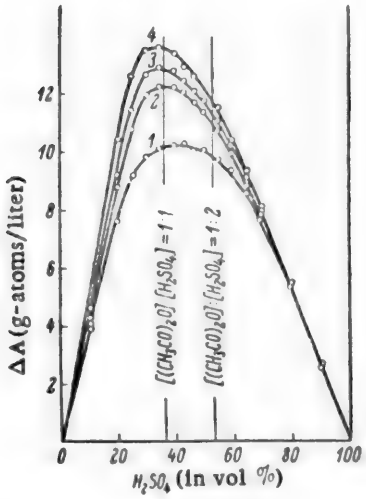

Fig. 3. Deviation of atomic concentration of the system $(CH_3CO)_2O$–H_2SO_4 from the additive value (ΔA); temperature 25°; 1) directly after mixing; 2) after 13 days; 3) after 38 days; 4) after 8 months.

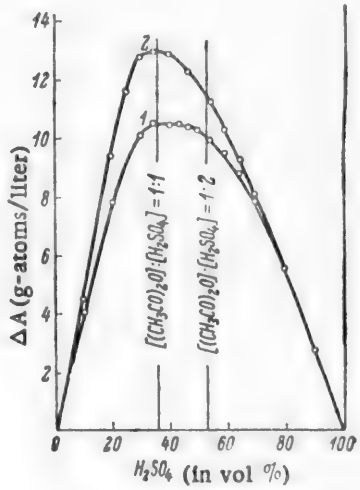

Fig. 4. Deviation of atomic concentration of the system $(CH_3CO)_2O$–H_2SO_4 from the additive value (ΔA); temperature 40.6°; 1) directly after mixing; 2) after 38 days.

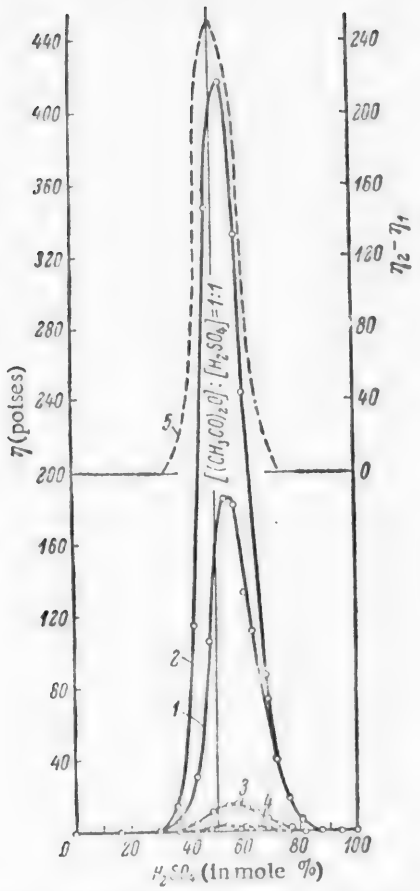

Fig. 5. Viscosity of the system $(CH_3CO)_2O-H_2SO_4$: 1) directly after mixing at 0°; 2) after 13 days at 0°; 3) after 13 days at 25°; 4) after 13 days at 40.6°; 5) graphical difference of isotherms 1 and 2.

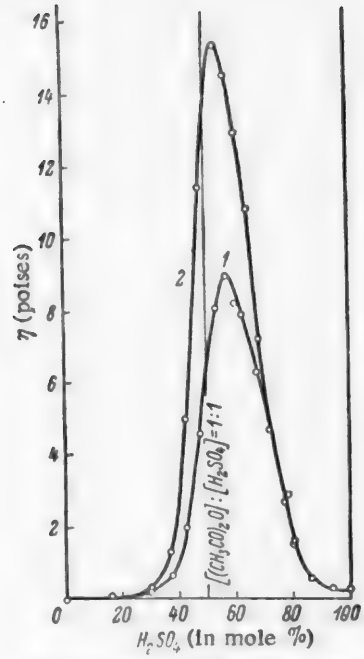

Fig. 6. Viscosity of the system $(CH_3CO)_2O-H_2SO_4$; temperature 25°; 1) directly after mixing; 2) after 13 days.

In Fig. 2 values of ΔA of the system after holding of the mixtures for 13 and 38 days at room temperature are given. The measurements were made at 0°. Similar data for 25° are given in Fig. 3, and for 40.6° after 38 days in Fig. 4.

In the process of carrying out the volume measurements at all temperatures an increase was observed in the deviation of the atomic concentration of the system from the additive value as the time of holding the mixtures from the moment of their preparation increased. A shift of the maximum ΔA in the direction of acetic anhydride with an increase in the time of holding the mixtures was clearly noted; i. e., in the direction of an equimolecular ratio of the components.

VISCOSITY OF THE SYSTEM

The results of a determination of the relative viscosity of the system are presented in Figs. 5 and 6. Since the viscosity of the same mixtures distinctly changes with a change in temperature, the graphic data are represented in the figures on different scales. Attention is attracted by the tremendous increase in viscosity of the mixtures in comparison with the viscosity of the starting components. This difference increases with a decrease in the temperature of measurement. As the time of holding the mixtures at room temperature increases, their viscosity increases rapidly. Thus, for example, the maximum viscosity of the system at 0° more than doubles after the mixtures are held for 13 days. The ratio of the viscosity of the mixtures after holding to the viscosity of freshly prepared mixtures increases with a decrease in the temperature of measurement.

The viscosity isotherms have a clearly expressed maximum reminiscent of a singular point, but shifted somewhat in the direction of a rational composition of the components. The greatest viscosity on the 0° isotherm (measurements made directly after preparation) is shown by the mixture containing 54.05% sulfuric acid. On the 25° isotherm with the system in the same condition the maximum viscosity corresponds to a mixture with 57.31 mole % H_2SO_4. Thus, at 0° the viscosity maximum is close to an equimolecular ratio of acetic anhydride and

sulfuric acid, and with an elevation in temperature the maximum is shifted somewhat in the direction of the more viscous component, sulfuric acid. The same situation is observed after 13 days holding.

When comparing the position of the maximum of the isotherms at the same temperature, but with a different time of holding the mixtures, notice should be taken of the slight shifting of the viscosity maximum in the direction of acetic anhydride. For the 0° isotherm this is expressed only in an unsymmetrical shifting of the two branches of the isotherm and in the greater proximity to the peak of the curve of the point with 57% sulfuric acid content. In Fig. 5 we have constructed Curve 5, which represents the graphical difference between Curves 2 and 1. The maximum in this curve corresponds to 50 mole % H_2SO_4.

INDEX OF REFRACTION

The index of refraction was measured directly after preparation of the mixtures at 25 ± 0.25°. The indicated accuracy in maintaining the temperature constant appeared to us to be sufficient, since the change in the system with time made it impossible to employ the fourth decimal place in the value of the index of refraction.

The isotherm for the index of refraction (Fig. 7) is arched away from the abscissa axis of the curve. In the interval 45-75 mole % of sulfuric acid it forms an almost flat section, so that it is difficult to decide to exactly what composition the maximum of such a form corresponds. We drew the curve for the deviation of the index of refraction from the additive value (Δn_D), plotting distances of the ordinate from the horizontal axis corresponding to the difference between the values of the index of refraction and the ordinates of the points on the straight line joining the values of the index of refraction of acetic anhydride and sulfuric acid (Fig. 7). The curve obtained is also arched away from the abscissa axis, but it has a perfectly definite maximum, the position of which corresponds to 50 mole % of sulfuric acid.

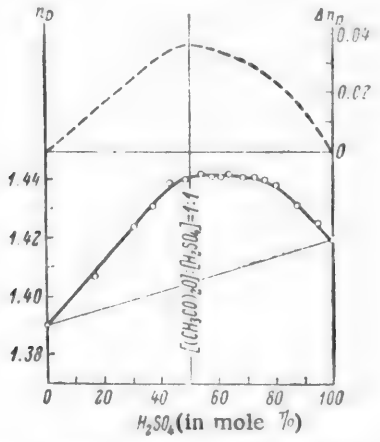

Fig. 7. Index of refraction of the system $(CH_3CO)_2O-H_2SO_4$; temperature 25°.

DISCUSSION OF RESULTS

The results of the volumetric measurements and the measurements of viscosity and index of refraction indicate a complex reaction process that changes with time in the system sulfuric acid—acetic anhydride. The changes taking place in the system directly after mixing of the components evidently are elicited by a rapidly proceeding reaction, since we have not noted that a change in the time of mixing at 0° affected the value of ΔA and the viscosity of the system to any appreciable extent. The processes taking place in the system in this condition are characterized by a flat maximum in ΔA. The position of the maximum on the abscissa axis is considerably closer to the ratio $[(CH_3CO)_2O]:[H_2SO_4] = 1:1$ than to $[(CH_3CO_2O]:[H_2SO_4] = 1:2$ or even 1:15.

The maximum viscosity in the system directly after preparation of the mixtures corresponds to a content of 57 mole % of sulfuric acid at 25° and 54 mole % of sulfuric acid at 0°. It is known that the maximum in the viscosity curves of irrational systems usually is shifted with a decrease in temperature in the direction of a rational composition of the reacting components. We therefore consider it possible that the viscosity isotherms of the system $(CH_3CO)_2O-H_2SO_4$ indicate the reaction of equimolecular quantities of acetic anhydride and sulfuric acid. The isotherm of the deviations in index of refraction from the additive value, which we obtained for the system directly after mixing, also reflect a process which is characterized by a ratio of the reacting components of 1:1. The peak of the maximum of the isotherm corresponds to 50 mole % of sulfuric acid.

On the basis of the experimental results obtained, and also the data from the literature cited above, we assume the existence in the system of an acid-base reaction. As a result of this reaction a complex compound of one mole of acetic anhydride with one mole of sulfuric acid is formed, which dissociates to an acetic anhydride cation and a hydrosulfate anion according to Equation (2) given above. This process causes appreciable positive deviations of the atomic concentration from the additive value with a maximum in the curve for ΔA vs. composition close to an equimolecular ratio and a sharp increase in the viscosity in the system, and also determines the shape of the isotherm for the deviation of the index of refraction from the additive value, with a maximum in the region of 50 mole % of sulfuric acid.

The process of splitting this cation with the formation of an acetyl ion and a molecule of acetic acid, which Gillespie [7] assumed proceeded practically to completion in the region of small concentrations of acetic anhydride [Equation (3)], evidently has no significance in the central portion of the system.

Actually, if we assume Process (3), it is necessary to assume further that the acetyl cation reacts with the strongest base in the system, the HSO_4^- ion, with the formation of acetylsulfuric acid, CH_3COOSO_3H, the formation of which has been assumed by many investigators after Franchimont [2]. No characteristics confirming the presence of this compound have been reported, however. Furthermore, no one has succeeded in isolating the hypothetical acetylsulfuric acid from the solution. According to the data of Russel and Cameron [5] the system sulfuric acid–acetic anhydride has a considerably greater hydrogen ion activity than that of sulfuric acid. It is not probable that acetylsulfuric acid, if we assume its formation in the system, would have such strong "ultra-acid" properties. Finally, on the basis of our observations [13] the formation of a mixed anhydride similar to acetylsulfuric acid in the system acetic anhydride–nitric acid is accompanied by an expansion of the system, i.e., ΔA has negative values. In the present case we observe, on the contrary, very considerable positive values of ΔA. Apparently acetylsulfuric acid is not formed in the system.

It is interesting to note that Gillespie [7], in order to explain a slight but distinct decrease in the freezing point depression with an increase in the concentration of acetic anhydride, assumed the existence in the solution of a certain amount of the cation of acetic anhydride $(CH_3CO)_2OH^+$.

The hypothesis of Leisten [8] concerning the formation of sulfur trioxide in the mixtures [Equations (6) and (7)] by the reaction of one mole of acetic anhydride with three moles of sulfuric acid does not agree with the experimental data obtained by us on the density, viscosity, and index of refraction of the system. It is completely probable that Leisten's equilibrium occurs in the region of a very great excess of sulfuric acid and loses its significance when the concentration of the latter compound decreases.

Thus, we rest with the hypothesis that a complex compound is formed in the system and dissociates to a considerable extent into $(CH_3CO)_2OH^+$ and HSO_4^- ions. A similar compound of benzoic anhydride with sulfuric acid is known in the solid state [6].

Furthermore, the process of sulfonation of the acetic anhydride with the formation of sulfoacetic acid apparently gradually takes place in the system.

SUMMARY

1. The density at 0, 25, and 40.6°, the viscosity at 0 and 25°, and the index of refraction at 25° have been determined in the system acetic anhydride–sulfuric acid directly after mixing of the components.

2. The increment in the atomic concentration in comparison with its additive value, the viscosity, and the index of refraction of the system acetic anhydride–sulfuric acid directly after mixing indicate a reaction in the system which takes place with the participation of one mole of acetic anhydride and one mole of sulfuric acid. A hypothesis is offered that this reaction leads to the formation of a complex product, which dissociates into an acetic anhydride cation and a hydrosulfate ion. In the process of formation of the addition product, the acetic anhydride fulfills the function of a base.

The density at 0 and 25° and the viscosity at 0, 25, and 40.6° of the system $(CH_3CO)_2O - H_2SO_4$ have been determined 13 days after the time of preparation of the mixtures, and also the density of the system at 0, 25 and 40.6° 38 days after the time of preparation. In these measurements a further increase in the atomic concentration and the viscosity of the system with time was observed. It was determined that there is a shift in the maxima of the atomic concentration and the viscosity in the direction of an equimolecular composition of the components. The change in the atomic concentration and the viscosity reflects a process of sulfonation, as a result of which sulfoacetic acid is formed in the system.

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THE SYSTEM ACETIC ANHYDRIDE – SULFURIC ACID

II. SYNTHESIS OF SULFOACETIC ACID AND VOLUMETRIC INVESTIGATION OF AN "ARTIFICIAL SYSTEM"

T. V. Mal'kova

Ivanovo Chemicotechnological Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2120-2124,
July, 1960
Original article submitted February 5, 1959

The formation of sulfoacetic acid in the system acetic anhydride–sulfuric acid has already been reported by Franchimont [1], who considered that all the sulfuric acid was converted to sulfoacetic acid when a mixture of acetic anhydride and sulfuric acid in the ratio 2:1 was heated to 120-130°. Stillich [2] isolated the sulfoacetic acid from a heated mixture of sulfuric acid and acetic anhydride in the form of its salt with 3-N-(p-nitrophenyl)-2-methyl-6-nitro-3,4-dihydroquinazoline.

Of the research during the last two decades, the following investigations are of interest: the investigation of the relationship of the pH of the medium to the amount of acetic anhydride added to the sulfoacetic acid [3], the study of the kinetics of the reaction producing the sulfoacetic acid [4], and the mechanism proposed for the formation of sulfoacetic acid in mixtures of acetic anhydride and sulfuric acid [5].

In order to verify the hypothesis that volume changes in the system $(CH_3CO)_2O-H_2SO_4$, when it is subjected to prolonged storage, are due to the formation of sulfoacetic acid, we prepared an "artificial system" from sulfoacetic acid, acetic acid, acetic anhydride, and sulfuric acid. The "artificial system" corresponded in composition to the system acetic anhydride–sulfuric acid under the conditions of the completed process of sulfonation with the formation of sulfoacetic acid.

The sulfoacetic acid was prepared by us by Stillich's [6] and Collmann's [7] method, by the reaction of monochloroacetic acid with sodium sulfite. According to the data in the literature, this method yields the acid free of impurities [6, 8]. For the synthesis we used monochloroacetic acid boiling over the range 184.5-186°.

In isolating the free sulfoacetic acid from its barium salt, we avoided the introduction of excess sulfuric acid. We analyzed the barium salt for its barium sulfate content and total barium content (the barium sulfate appeared in the salt in the synthetic process as a result of sulfate impurity in the sodium sulfite). To an aqueous suspension of barium sulfoacetate was added the exactly calculated amount of sulfuric acid required for liberation of the sulfoacetic acid. After several hours stirring, the barium sulfate that had precipitated was filtered off. The absence of Ba^{2+} and SO_4^{2-} ions was checked in the filtrate. Then the filtrate was evaporated on a water bath. When the filtrate attained the consistency of castor oil, it was seeded by the introduction of a crystal of sulfoacetic acid. The crystals that precipitated were quickly filtered in vacuum, dried with sulfuric acid, and air was passed through the filter. The precipitate on the filter was washed twice with ether.

The crystals of sulfoacetic acid were very hygroscopic and deliquesced in the air. To remove the remaining water of crystallization, the precipitate was concentrated in vacuum at 115-152°. As the last amounts of water were lost, the acid darkened noticeably and crystallized when it solidified, even when it was diluted with an equimolecular quantity of acetic acid. We therefore decided to use in our work sulfoacetic acid containing 0.5 mole of water. This acid contained 0.5 mole of water and had a concentration of 94% (93.98% according to data from a titration with 0.1 N NaOH with phenolphthalein, and 94.16% according to its sulfuric acid content).

We set up as a goal the preparation of mixtures with sulfoacetic acid that would correspond in composition to the mixtures of acetic anhydride and sulfuric acid under final conditions of the reaction between them to form sulfoacetic acid. The amount of acetic acid in these mixtures was equimolecular with the sulfoacetic acid. The composition of the mixtures was expressed in volume percent of the starting components—sulfuric acid and acetic anhydride. The water which was introduced with the sulfuric acid was not taken into account in calculating the percent composition. Thus, a mixture corresponding to 36 vol % of sulfuric acid (Table 1) consisted of an equimolecular mixture of sulfoacetic acid and acetic acid. To prepare mixtures corresponding to a larger relative amount of sulfuric acid, we added to the indicated mixture the calculated amount of sulfuric acid. To prepare mixtures corresponding to a smaller amount of H_2SO_4 we added acetic anhydride to this mixture.

TABLE 1. Density (d) and Deviation of Density from the Additive Value (Δd) of a System "Artificially" Prepared from Sulfoacetic Acid at 25°

Composition of mixtures (in vol %)		d	d_i	Δd
H_2SO_4	$(CH_3CO)_2O$			
0.00	100.00	1.0721	1.0721	0.0000
15.00	85.00	1.2426	1.1812	0.0614
25.00	75.00	1.3651	1.2511	0.1150
30.00	70.00	1.4236	1.3885	0.1385
36.00	64.00	1.4890	1.3253	0.1637
40.01	59.99	1.5200	1.3553	0.1647
45.31	54.69	1.5588	1.3953	0.1635
50.02	49.98	1.5915	1.4311	0.1604
60.01	39.99	1.6560	1.5111	0.1449
70.01	29.99	1.7115	1.5866	0.1249
80.01	19.99	1.7585	1.6666	0.0919
100.00	0.00	1.8314	1.8314	0.0000

In calculating the volume changes in the system we considered an equimolecular mixture of sulfoacetic acid and acetic acid as an equimolecular mixture of acetic anhydride and sulfuric acid. The ideal density of the system (d_i) was determined as the quotient from the division of the sum of the amounts by weight of sulfuric acid, acetic anhydride, and water constituting the given mixture by the sum of the volumes which these amounts occupied. Thus, Δd represents a value characterizing the formation of sulfoacetic acid from acetic anhydride and sulfuric acid. The deviations of the density obtained from the additive value was compared with the corresponding values in the system $(CH_3CO)_2O-H_2SO_4$.

In Table 1 the composition of the mixtures of the "artificial system" prepared from sulfoacetic acid, the density of the mixtures, and the values of d_i and Δd are given.

In Fig. 1, Curve 4 represents the isotherm for Δd of the system prepared from sulfoacetic acid at 25°; Curves 1-3 are the isotherms for Δd of the system acetic anhydride—sulfuric acid under various conditions.

It was natural to expect that the water which was introduced into the mixture together with the sulfoacetic acid would affect the shape of the isotherm for Δd of the "artificial system." In order to evaluate its effect, we added water to the mixtures of the system $(CH_3CO)_2O-H_2SO_4$ which had been stored for a long time. The water was added to each mixture in a $\frac{1}{2}$ molar amount with respect to the amount of sulfoacetic acid which might be formed in the mixture under conditions of completion of the sulfonation process. Thus, in the case of mixtures in which the number of moles of sulfuric acid exceeded the number of moles of the anhydride, water was added in half-molar amount with respect to the acetic anhydride. On the other hand, water was added in half-molar amount with respect to the sulfuric acid to those mixtures in which the number of moles of acetic anhydride exceeded the number of moles of sulfuric acid. The density of the mixtures prepared, diluted and undiluted, was determined at 25° (Table 2, Fig. 2).

A comparison of the isotherms for Δd of the system $(CH_3CO)_2O-H_2SO_4$ at different times and the isotherms for Δd of the "artificial system" permitted the following observations.

The isotherms of the two systems passed through a maximum. The shape and position of the maximum of the curves was not the same if the system acetic anhydride-sulfuric acid was measured directly after mixing. On the other hand, after the mixtures of acetic anhydride and sulfuric acid had been held at room temperature, the shape of the isotherms for the two systems became identical. The maximum Δd for both systems under these conditions corresponded to 40 vol % of sulfuric acid. The absolute values of Δd for all mixtures in the "artificial system" were somewhat larger than in the system $(CH_3CO)_2O-H_2SO_4$. This indicates that the process of sulfonation was not yet completed at the time of the last measurements in the system (8 months from the time of preparation of the mixtures). Furthermore, slight side processes which increase as the temperature is raised apparently take place in the system. This is indicated by the red-brown color which the mixtures acquired in the course of time.

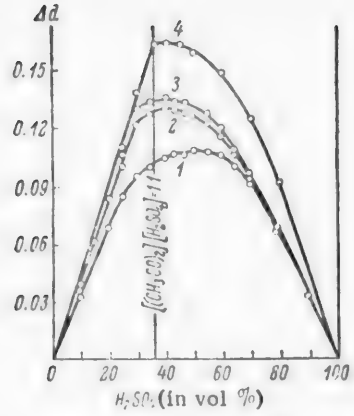

Fig. 1. Deviation of density from the additive value for the "artificial system" and the system $(CH_2CO)_2O-H_2SO_4$; temperature 25°: 1) Δd of system $(CH_3CO)_2O-H_2SO_4$ directly after preparation; 2) Δd after 38 days; 3) Δd after 8 months; 4) Δd of "the artificial system."

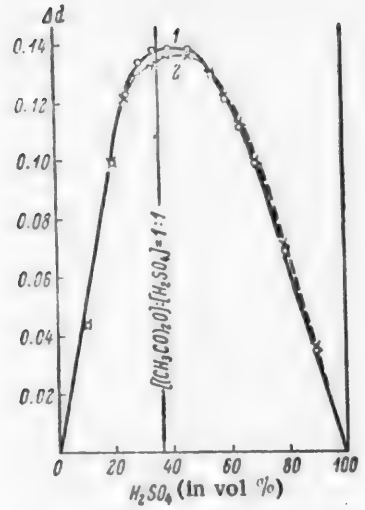

Fig. 2. Deviation of density from the additive value for the system $(CH_3CO)_2O-H_2SO_4$; temperature 25°; 1) Δd without dilution; 2) Δd after dilution with water.

TABLE 2. Deviation of Density from the Additive Value (Δd) for the System $(CH_3CO)_2O-H_2SO_4$ after Prolonged Holding before Dilution with Water and after Dilution at 25°

Composition of mixture* (in vol %)		Before dilution with water		After dilution with water	
H_2SO_4	$(CH_3CO)_2O$	d	Δd	d	Δd
0.00	100.00	1.0721	0.0000	—	—
10.21	89.79	1.1932	0.0435	1.1898	0.0447
19.76	80.24	1.3213	0.0991	1.3144	0.0995
24.81	75.19	1.3834	0.1229	1.3717	0.1218
29.62	70.38	1.4304	0.1334	1.4127	0.1301
34.30	65.70	1.4701	0.1375	1.4469	0.1328
39.58	60.42	1.5118	0.1392	1.4881	0.1359
46.43	53.57	1.5634	0.1388	1.5405	0.1367
54.59	45.41	1.6168	0.1302	1.5963	0.1300
59.23	40.77	1.6433	0.1214	1.6244	0.1222
64.17	35.83	1.6703	0.1110	1.6525	0.1118
69.26	30.74	1.6970	0.0990	1.6805	0.0997
79.34	20.66	1.7434	0.0688	1.7322	0.0707
89.93	10.07	1.7893	0.0343	1.7837	0.0360
100.00	0.00	1.8314	0.0000	—	—

Dilution with water of the mixtures of acetic anhydride and sulfuric acid after prolonged standing (Fig. 2) did not lead to an essential change in the shape of the isotherm and the absolute value of Δd. We therefore considered it possible to compare the isotherms 1-3 with isotherm 4 (Fig. 1).

It is interesting that the addition of water to mixtures containing less than 20 vol % or more than 55 vol % of sulfuric acid was accompanied by a slight increase in Δd. Addition of water to mixtures lying within this concentration range was accompanied by a noticable decrease in Δd. This decrease may have been due to the fact that the reaction of sulfoacetic acid with water is not accompanied by a sufficient contraction effect to exceed the opposite effect caused by the decrease in the number of molecules of sulfoacetic acid per unit volume because of the introduction of the water. It also is possible that this decrease in volume is explained by the decomposition of a reaction product of sulfoacetic acid with acetic acid or with some other component of the system when water is added.

*For diluted mixtures the percentages were nominal, without taking into account the amount of water.

The volume changes observed when sulfoacetic acid containing 0.5 mole of water was mixed with acetic acid show somewhat greater contraction (according to data from a previous calculation) than that which might be expected even under the conditions where all of the water contained in the system reacts with the acetic acid to form hydrates. It therefore may be assumed that the acetic acid combines in some way with the sulfoacetic acid. This assumption explains the fact reported in the literature that even heating acetic anhydride with sulfuric acid to 160° is insufficient to drive off all the acetic acid from it [1].

SUMMARY

1. The density at 25° and the calculated deviations of the density from the additive value have been determined in an "artifical system" which was made up from sulfoacetic acid (containing 0.5 mole of water), acetic acid, acetic anhydride, and sulfuric acid and corresponded in composition to the system acetic anhydride–sulfuric acid in the condition where the formation of sulfoacetic acid had been completed.

Investigation of the shape of the isotherm for the deviation of the density from the additive value for the "artificial system" confirmed that the principal process in the system $(CH_3CO)_2O-H_2SO_4$ during a prolonged holding period was the formation of sulfoacetic acid.

2. The density at 25° was determined and the isotherm for the deviation of the density from the additive value was constructed for the system $(CH_3CO)_2O-H_2SO_4$ with water added in an amount corresponding to half-molar with respect to the amount of sulfoacetic acid formed in the system. Dilution of the system with the indicated amounts of water slightly changed the deviation of the density from the additive value (Δd) and in the main did not change the form of the isotherm.

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THERMAL ANALYSIS OF THE TERNARY SYSTEM ACETAMIDE – ACETIC ACID – PHENYLACETIC ACID

V. F. Chesnokov and I. M. Bokhovkin

Arkhangel'skii Forestry Technological Station
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2124-2127,
July, 1960
Original article submitted June 30, 1959

We have investigated the ternary system acetamide–acetic acid–phenylacetic acid by the thermal method. We set up as our problem the determination of the behavior of acetamide together with two organic acids. Acetamide has a high dielectric permeability in the fused state (60.3 at 80°) and in connection with this it should readily dissolve organic acids and show a polarizing effect on them.

EXPERIMENTAL

The system was studied by the polytherm method; by this process we determined the temperature at which the last crystals disappeared.

The starting materials were purified as follows: acetamide by recrystallization from benzene, m.p. 79.5°; acetic acid by freezing out, m.p. 16.6°. Phenylacetic acid of chemically pure grade, m.p. 75°, was used.

BINARY SYSTEMS

The system acetamide–acetic acid was investigated with respect to its fusion by V. L. Albanskii [1] and this was repeated by us. The existence in it of a compound with a 1:1 composition with a hidden maximum was established. The eutectic points lay at 28.5 mole % of acetamide and -17° and at 48.5 mole % of acetamide and -2.4°.

The system acetic acid–phenylacetic acid had been studied by us previously [2] and was characterized by a eutectic point with m.p. +2° at 23 mole % of phenylacetic acid.

The system acetamide–phenylacetic acid was studied by us. The fusion diagram is characterized by a eutectic with m.p. 3° at 47 mole % of acetamide. The data for this system are given in the table and Fig. 1.

SECTIONS THROUGH THE TERNARY SYSTEM

To develop the surface of crystallization of the ternary system, we investigated 11 sections in the directions indicated in Fig. 5. The numbers of the sections correspond with the numbers of the curves in Figs. 2-4.

In investigating the sections 2, 3, and 4 in the region of the eutectic points a_1 (Fig. 3, 4), and also section 8 at the point a (Fig. 2), we observed strong supercooling. The liquid became viscous and occluded air, which hampered the determination. In sections 5, 6, and 7 in the region of temperatures close to the eutectic points formation of crystals did not occur. The liquid became very viscous at first, and then, upon further cooling, solidified to a transparent, glassy mass.

Therefore, in the indicated sections close to the eutectic points we recorded not the temperatures of disappearances of the last crystals, but the softening temperatures of the mixtures. In Figs. 2-4, and also in the diagram of the fusion isotherms of the ternary system (Fig. 5) these regions are indicated by broken lines.

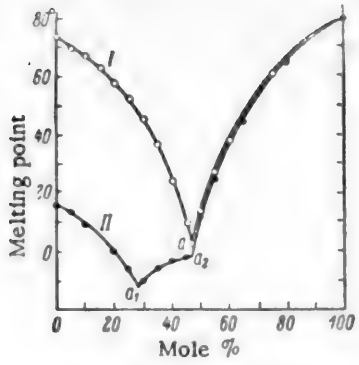

Fig. 1. Fusion curves: I) phenylacetic acid – acetamide; II) acetic acid–acetamide.

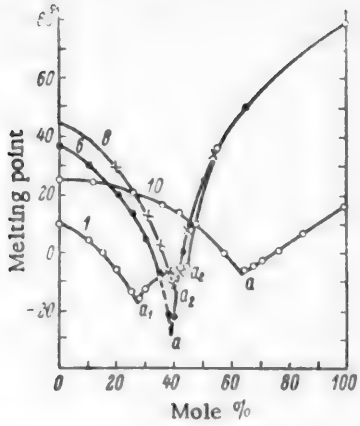

Fig. 2. Curves of crystallization in sections 1, 6, 8, 10.

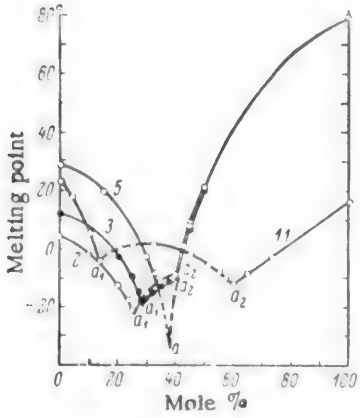

Fig. 3. Curves of crystallization in sections 2, 3, 5, 11.

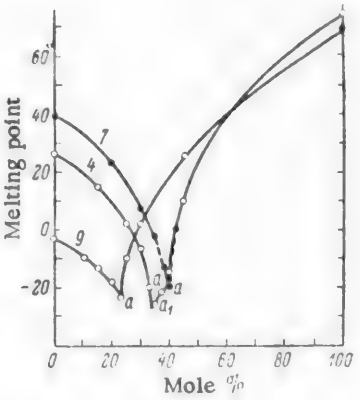

Fig. 4. Curves of crystallization in sections 4,7, 9.

Melting Points of Binary Mixtures in the System Phenylacetic Acid–Acetamide

Mole % CH_3CONH_2	Melting Point
0.00	74.0°
5.0	69.5
10.0	66.6
15.0	62.5
20.0	57.5
25.0	52.3
30.0	45.2
35.0	36.3
40.0	24.0
45.0	9.5
50.0	14.0
55.0	27.5
60.0	38.2
75.0	61.0

On the basis of our data we constructed a fusion diagram of the ternary system acetamide–acetic acid–phenylacetic acid and plotted the isotherms for each 10° (Fig. 5).

The fusion diagram obtained includes 4 fields of crystallization: three fields for the pure components and one field for the compound $CH_3CONH_2 \cdot CH_3COOH$.

In the system there are two triple eutectic points: E_1 with 36.5 mole % acetamide, 37 mole % acetic acid, and 26.5 mole % phenylacetic acid at -38°, and E_2 with 26 mole % acetamide, 19 mole % acetic acid, and 55 mole % phenylacetic acid at -25°.

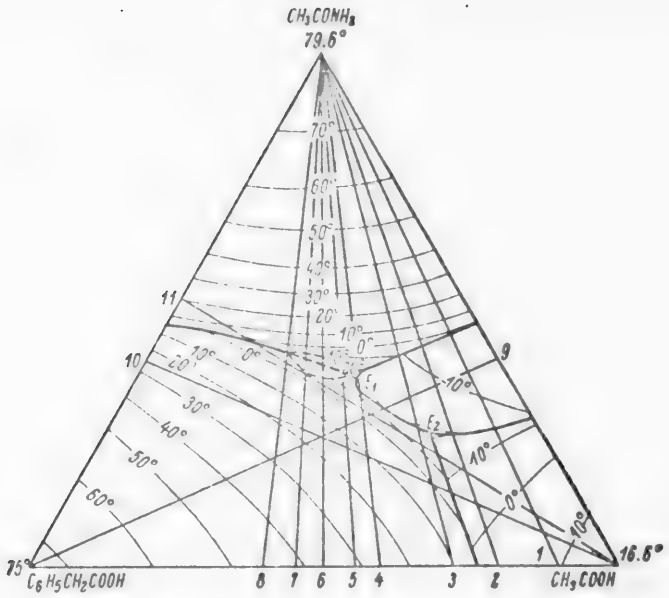

Fig. 5. Structural diagram of ternary system.

SUMMARY

1. The system acetamide–acetic acid–phenylacetic acid has been investigated by the thermal method.

2. The absence of a chemical reaction in the binary system acetamide–phenylacetic acid has been established.

3. A compound found in the binary system acetamide–acetic acid exists in the ternary system, where its region of crystallization is reduced as the phenylacetic acid content increases.

4. It has been established that acetamide in the presence of acetic and phenylacetic acids with approximately equal proportions of the components does not give a crystalline structure with easily differentiated crystalline particles, but forms a continuous, solid, transparent, glassy mass, which passes over to a liquid condition with an increase in temperature. This phenomenon is associated with the sharply increasing viscosity of the medium at temperatures close to the freezing point.

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•Original Russian pagination. See C. B. translation.

HEATS OF MIXING DIOXANE WITH CHLOROFORM AND o-TOLUIDINE

O. A. Osipov, M. A. Panina, and E. S. Yagubyan

Rostov-on-Don State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2127-2130, July, 1960

Original article submitted July 6, 1959

Investigators have shown considerable interest in dioxane because it is a good solvent for various classes of organic and inorganic compounds. The presence in dioxane of two atoms of oxygen which can be electron donors is responsible for its capacity for complex formation.

In the present work we present the results of a determination of the heats of mixing of dioxane with chloroform and o-toluidine. The method of determining the heats of mixing has been described previously [1, 2]. The components were purified in the following manner. The dioxane was distilled after prolonged storage over calcium chloride. The distillate, which was condensed over the range 100.5-100.7°, was frozen out at 6-7°. Then the crystals were freed of the liquid phase and were transferred to a flask with metallic sodium. After standing for 10 days and being boiled for 6 hours with the metallic sodium, the dioxane was distilled. For the work, the fraction boiling at 101.3-101.5° (757 mm) was collected. The dioxane purified in this way froze completely at 12.2° and had the constants d_4^{20} 1.0351 and n_D^{20} 1.4228. The o-toluidine, after drying with potassium hydroxide, was fractionally distilled. For the work, the fraction boiling at 199.5-200.1° (755 mm), d_4^{20} 0.9984, n_D^{20} 1.5726 was used. The washed and dried chloroform after 2 distillations had the b.p. 61.1° (750 mm), d_4^{20} 1.4893, n_D^{20} 1.4457. The results of the determination of the heats of mixing of dioxane with chloroform are given in Table 1 and Fig. 1.

TABLE 1. Heats of Mixing of Dioxane with Chloroform

$C_4H_8O_4$ (in mole %)	Q (cal/ /mole of mixture)	Q_I (cal/ /mole of dioxane)	Q_{II} (cal/ /mole of chloroform)
0.0	0	0	0
18.5	361.3	1950	443
21.5	390.8	1818	498
37.0	485.8	1313	771
43.5	496.5	1141	868
48.0	488.9	1020	940
52.0	460.9	886	960
59.0	413.6	701	1009
70.0	305.0	438	1018
79.0	228.3	288	1087
100.0	0	0	0

TABLE 2. Heats of Mixing of Dioxane with o-Toluidine

$C_2H_8O_2$ (in mole %)	Q (cal/ /mole of mixture)	Q_I (cal/ /mole of dioxane)	Q_{II} (cal/ /mole of o-toluidine)
0.00	0.0	0	0
20.00	167.0	835	209
30.00	226.4	755	334
40.00	270.8	677	452
50.00	290.7	582	582
60.00	268.2	447	671
70.00	216.9	310	723
80.00	155.6	195	778
100.00	0.0	0	0

From the data presented it can be seen that the curve for the heats of mixing of dioxane with chloroform passes through a maximum corresponding to 43.44 mole % of dioxane, i.e., somewhat in the direction of the composition of the compound $C_4H_8O_2 \cdot CHCl_3$, which is formed in the system. It is known that such a deviation indicates that the complex compound obtained is subject to thermal dissociation into the components. Frequently the degree of decomposition is so considerable that it appears

impossible to accurately establish the composition of the compound from the maximum in the curve of the heats of mixing. Consequently, in a number of cases for irrational systems the results of the measurements of the heats of mixing expressed in calories per mole of mixture permit a statement of the presence of a chemical reaction between the components, but cannot reliably indicate the composition of the compound.

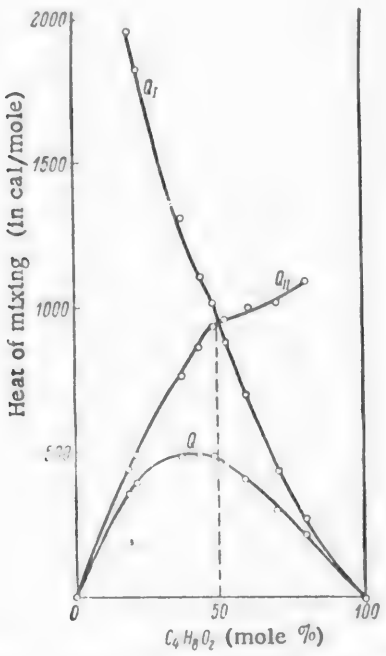

Fig. 1. Heats of mixing of dioxane with chloroform; explanation in the text.

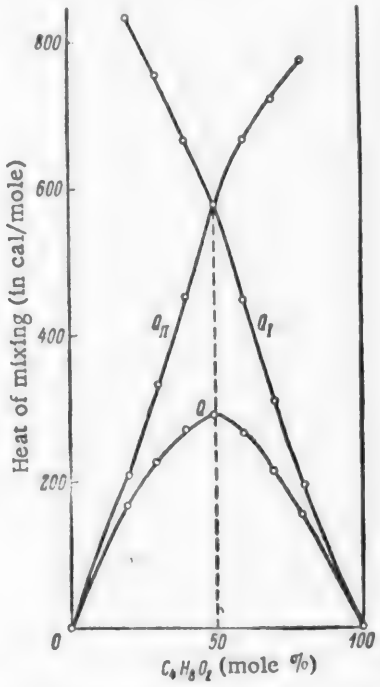

Fig. 2. Heats of mixing of dioxane with o-toluidine; explanation in the text.

In work by one of us with Yu. A. Lysenko [3] it has been shown that for a system in which a reaction occurs

$$A + sB \rightleftarrows AB_s,$$

more reliable evidence of reaction between the components can be obtained by calculation of the heat effects for 1 mole of each component of the system. The results of such calculations for the system dioxane–chloroform are given in Table 1 and Fig. 1. As can be seen in Fig. 1, the point of intersection of the curves corresponds to an equimolar ratio of the components. Thus, the calculation of the heats of mixing for 1 mole of each of the components of the system gives a more descriptive picture of the chemical reaction and permits the conclusion that in the system studied by us a compound of the composition $C_4H_8O_2 \cdot CHCl_3$ is formed.

In Table 2 and Fig. 2 the results of the measurements of the heats of mixing of dioxane with o-toluidine are given. The heat effects calculated both for 1 mole of the mixture and for 1 mole of each of the components show that a compound of the composition $C_4H_8O_2 \cdot C_6H_4CH_3NH_2$ is formed in the system.

Thus, the isotherms of the heats of mixing indicate the formation in the systems dioxane–chloroform and dioxane–o-toluidine of molecular compounds originating, probably, as a result of a hydrogen bond. The small values of the heats of mixing indicate that the complex compounds obtained are strongly dissociated. We also observe the same picture for the system dioxane–aniline [4], where the maximum heat of mixing of the components, used in the ratio 1:1, is 354.6 cal/mole of mixture at 24°. With an increase in the temperature its value decreases. For example, at 40° it is 339.3, and at 60° it is 289.8 cal/mole of mixture.

The presence of a chemical reaction in the systems dioxane–chloroform and dioxane–toluidine is indicated by the results of an investigation of the electrical properties of the systems carried out by one of us together with I. K. Shelomov [5]. These data show that the maximum deviations in the dielectric constant, polarization, and dipole moment occur at a composition corresponding to the complex compound formed.

SUMMARY

1. The heats of mixing of dioxane with chloroform and o-toluidine have been determined for the entire concentration range.

2. It has been shown that for a system with a chemical reaction it is expedient to carry out a calculation of the heats of mixing for 1 mole of each of the components.

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INVESTIGATION OF THE LIQUID-VAPOR PHASE EQUILIBRIA IN THE SYSTEMS FORMED BY $TiCl_4$ WITH MONO- AND TRICHLOROACETYL CHLORIDES

G. V. Seryakov, S. A. Vaks, and L. S. Sidorina

Scientific Research and Planning Institute for the Rare Metal Industry

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2130-2133, July, 1960
Original article submitted June 10, 1959

According to data in the literature, technical titanium tetrachloride prepared by the chlorination of oxide materials with chlorine in the presence of carbon may contain chloroacetyl chlorides [1, 2]. In the present work we have investigated the liquid-vapor phase equilibria in the binary systems $TiCl_4-CH_2ClCOCl$ and $TiCl_4-CCl_3COCl$ in order to determine the efficiency of rectification for the purification of titanium tetrachloride from these contaminants. Besides the study of the equilibria mentioned, we have determined the vapor pressures of the individual mono- and trichloroacetyl chlorides and also that of titanium tetrachloride at different temperatures.

The mono- and trichloroacetyl chlorides were prepared by the action of thionyl chloride on the corresponding chloroacetic acids. The acid chlorides obtained were purified by fractional distillation twice on a cap column with an efficiency of approximately 10 theoretical plates at a reflux value of 10. For the investigation we used fractions that distilled over at constant temperatures within limits of 0.1°. Pure titanium tetrachloride was prepared from the technical product by two fractional distillations on the column mentioned. The first fractionation was combined with the operation of chemical purification of the titanium tetrachloride from vanadium, for which purpose copper turnings in the amount of 10% by weight of the titanium tetrachloride were placed in the pot of the column. After operating the column with complete return reflux for 2 hours, collection of the distillate was started with a reflux value of about 10. The fraction of $TiCl_4$ that distilled off at constant temperature within limits of 0.2° was refractionated. For the investigation we selected a fraction of titanium tetrachloride that distilled off in the second fractionation within a temperature interval of ≤0.1°.

The products thus purified were colorless liquids. The boiling points of the $TiCl_4$, $CH_2ClCOCl$, and CCl_3COCl at 760 mm were 136.5, 106.0, and 118.1°, respectively. The investigations of the liquid-vapor phase equilibria and the determination of the vapor pressures of the pure components were carried out in a recirculating apparatus by the methods described in detail in reference [3]. Samples of the vapor condensate and the liquid phase were analyzed for carbon by the combustion method. The amount of carbon found was calculated to the corresponding chloroacetyl chloride.

In the process of boiling mixtures of $TiCl_4$ with the chloroacetyl chlorides we at first observed yellowing and then darkening of the solutions. It should be noted, however, that the appearance of the color was not accompanied by a change in the boiling point of the solutions when they were boiled for 2 hours. It was mainly the circulating liquid phase that darkened on boiling, while the condensate of the distillate was only slightly colored. This phenomenon apparently can be explained by the formation of nonvolatile products as a result of the reaction of the components with one another. It therefore is possible that the compositions found by us for the liquid and the vapor differ somewhat from the equilibrium values.

The data on the boiling points of the $TiCl_4$, $CH_2ClCOCl$, and CCl_3COCl are given in Table 1 and shown in Fig. 1 with the coordinates log P vs. 1/T. The results obtained for titanium tetrachloride agree well with the latest data in the literature [4].

TABLE 1. Boiling Points of $TiCl_4$, $CH_2ClCOCl$, and CCl_3COCl at Different Pressures

$TiCl_4$		$CH_2ClCOCl$		CCl_3COCl	
P (mm Hg)	t	P (mm Hg)	t	P (mm Hg)	t
156	85°	155	62.5	200	76.1
185	89.0	209	69.2	302.4	88.0
188	90.8	303	79.0	412	97.4
310	105.6	516	94.1	514	106.5
427	116.2	640	100.7	760	118.1
610	128.4	762	106.2	842	121.9
763	136.8	819	108.5		
817	139.5				

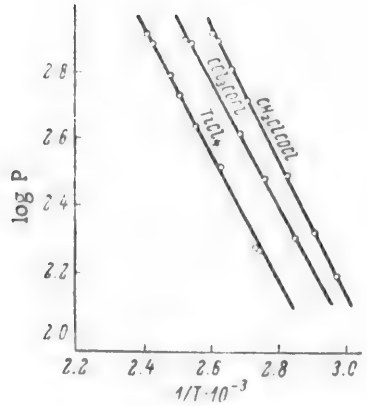

Fig. 1. Vapor tensions of $TiCl_4$, $CH_2ClCOCl$, and CCl_3COCl at different temperatures.

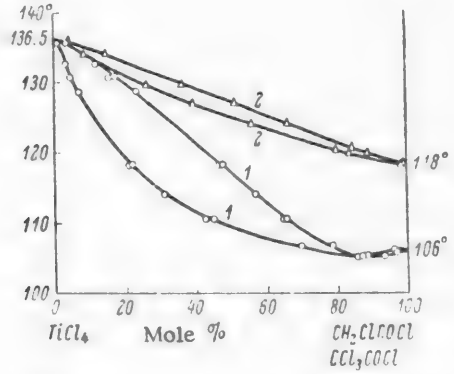

Fig. 2. Diagrams of boiling point vs. composition for the systems $TiCl_4-CH_2ClCOCl$ and $TiCl_4-CCl_3COCl$: 1) $TiCl_4-CH_2ClCOCl$; 2) $TiCl_4-CCl_3COCl$.

The vapor pressures of the compounds investigated within the temperature interval studied can be expressed by the following equations:

$$\lg P_{TiCl_4} = -\frac{1961}{T} + 7.669; \quad \lg P_{CH_2ClCOCl} = -\frac{2049}{T} + 8.287;$$

$$\lg P_{CCl_3COCl} = -\frac{1845}{T} + 7.594.$$

The molar heats of vaporization and the Truton constants calculated by means of these equations are, respectively: 8971 cal/mole and 22.0 for $TiCl_4$, 9374 cal/mole and 24.7 for $CH_2ClCOCl$, and 8441 cal/mole and 21.6 for CCl_3COCl. The anomalously high value of the Truton constant for $CH_2ClCOCl$ should be noted. This indicates the presence in this liquid of a stronger intermolecular reaction than in $TiCl_4$ and CCl_3COCl.

The liquid-vapor equilibria in the systems $TiCl_4-CH_2ClCOCl$ and $TiCl_4-CCl_3COCl$ were investigated at a pressure of 760 mm. The experimental data are given in Table 2, and also in the "boiling point–composition" and "liquid composition–vapor composition" diagrams (Figs. 2 and 3). From the data obtained, the relative volatilities were calculated and diagrams of "relative volatility vs. liquid composition" were constructed (Fig. 4).

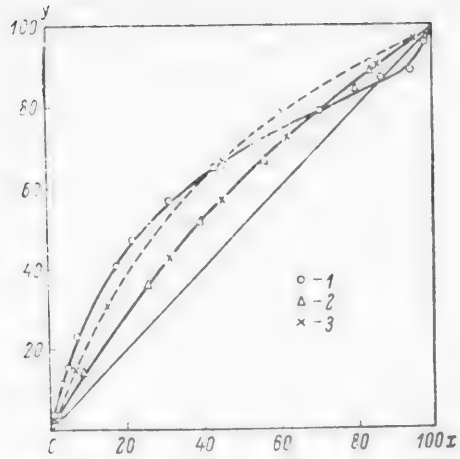

Fig. 3. Diagrams of liquid composition vs. vapor composition for the systems $TiCl_4$ – $CH_2ClCOCl$ and $TiCl_4$ – CCl_3COCl; 1) $TiCl_4$ – $CH_2ClCOCl$; 2) $TiCl_4$ – CCl_3COCl; 3) points of curves of the ideal systems calculated from the vapor pressure of the pure components.

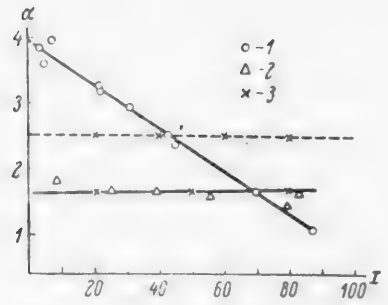

Fig. 4. Diagrams of liquid composition vs. relative volatility for the systems $TiCl_4$ – $CH_2ClCOCl$ and $TiCl_4$ – CCl_3COCl; 1) $TiCl_4$ – $CH_2ClCOCl$; 2) $TiCl_4$ – CCl_3COCl; 3) points of curves of the ideal systems.

From the data obtained it follows that the system $TiCl_4$ – $CH_2ClCOCl$ differs greatly from the ideal. In it, apparently, there is an azeotrope with a minimum boiling point*. The azeotropic mixture contains 87 mole % of $CH_2ClCOCl$ and boils at 105°. In the region of compositions up to 41 mole % of the acid chloride in this system a positive deviation from Raoult's law is observed. This circumstance facilitates purification of titanium tetrachloride from monochloroacetyl chloride by fractional distillation, which can be carried out without special difficulties as a result of the comparatively high relative volatility of the components (~3.9). Judged by the character of the relationship $\alpha = f(x)$, there should be no azeotrope in the system under consideration in the concentration region adjacent to pure $TiCl_4$. When technical titanium tetrachloride is purified by rectification, the distillate of $SiCl_4$ will contain chloroacetyl chloride.

TABLE 2. Composition of Liquid and Vapor and Relative Volatilities in the Systems $TiCl_4$ – $CH_2ClCOCl$ and $TiCl_4$ – CCl_3COCl at 760 mm Pressure

System $TiCl_4$–$CH_2ClCOCl$				System $TiCl_4$–CCl_3COCl			
t	$CH_2ClCOCl$ content		Relative Volatility* $\alpha = \frac{y}{1-y} : \frac{x}{1-x}$	t	CCl_3COCl content		Relative Volatility $\alpha = \frac{y}{1-y} : \frac{x}{1-x}$
	in liquid (in mole %) (100 x)	in vapors (in mole %) (100 y)			in liquid (in mole %) (100 x)	in vapors (in mole %) (100 y)	
136.5°	0	0	—	136.5°	0	0	—
135.8	1.12	3.84	—	136.0	1.595	3.73	—
135.5	1.36	4.01	—	134.2	8.500	14.40	1.808
132.8	3.28	11.55	3.8490	129.7	25.45	36.20	1.662
130.9	4.90	15.67	3.5950	127.2	39.30	51.60	1.640
128.8	7.20	23.50	3.9625	124.2	55.80	66.00	1.540
118.5	21.50	47.20	3.2600	120.5	79.65	84.60	1.405
118.3	22.05	47.30	3.1736	119.9	83.70	89.00	1.576
114.1	31.20	57.00	2.9256	118.3	99.00	99.30	—
110.6	45.10	65.80	2.3250	118.0	100.00	100.00	—
106.8	70.00	78.50	1.6040				
105.2	86.00	87.50	1.1400				
105.3	93.50	89.00	0.563				
105.8	97.00	96.50	0.854				
106.0	100.00	100.00	—				

* The relative volatility for compositions of the system which were adjacent to the pure components were not calculated, since the values obtained in this region would be inaccurate.

* The possibility of formation in this system of a chemical compound whose boiling point corresponds to this minimum seems improbable to us.

The presence of the azeotrope in the system $TiCl_4$–$CH_2ClCOCl$ may decrease the efficiency of thorough separation of $SiCl_4$ from the titanium tetrachloride by rectification, since the difference between the boiling point of the indicated azeotrope (105°) and $SiCl_4$ (57°) is considerably less than the difference in boiling point of $TiCl_4$ (136°) and $SiCl_4$. Therefore, before carrying out "thorough" separation of silicon tetrachloride by rectification, it is expedient to make a preliminary purification from chloroacetyl chloride by chemical means.

The system $TiCl_4$–CCl_3COCl, in contrast to the foregoing, did not differ practically from the ideal. As can be seen from the data presented, the relative volatility of the components in this system is comparatively small, about 1.5. It therefore is considerably more difficult to free the titanium tetrachloride of trichloroacetyl chloride than of monochloroacetyl chloride. Taking into consideration also the possibility of a negative effect of $CH_2ClCOCl$ on the "thorough" separation of $SiCl_4$ by rectification, it is best to recommend chemical means of separation for the removal from $TiCl_4$ of the chloroacetyl chlorides mentioned.

SUMMARY

1. The vapor tensions of titanium tetrachloride and of mono- and trichloroacetyl chlorides at different temperatures have been determined

2. The liquid-vapor phase equilibria in the binary systems formed by $TiCl_4$ with mono- and trichloroacetyl chlorides have been studied. In the first system, there apparently is an azeotrope containing 87 mole % of $CH_2ClCOCl$ with a boiling point of 105°. The second system shows almost no difference from the ideal.

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*Original Russian pagination. See C. B. translation.

TRANSALKYLATION REACTIONS IN A SERIES OF ELEMENTS OF THE THIRD AND FOURTH GROUPS (Al, B, Zn, Mg)

L. I. Zakharkin and O. Yu. Okhlobystin

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2134-2138, July, 1960
Original article submitted July 8, 1959

In recent years organoaluminum and organoboron compounds have become of especial interest because of their practical significance. During this period a number of new methods of preparing these compounds have been developed which have made them available even for commercial production; these methods include direct synthesis of α-aluminum trialkyls from aluminum, hydrogen, and α-olefins, and also synthesis by means of displacement [1]; in the case of the organoboron compounds, methods of synthesis from olefins and diborane (in the form of free diborane or as complexes of it with amines, and also as a mixture of $NaBH_4 + AlCl_3$ [2]) have been employed. A method has been developed for going from organoaluminum compounds to organoboron compounds by means of exchange reactions of aluminum trialkyls with a number of inorganic derivatives of boron, and also a method of synthesis of diborane through the boron trialkyls obtained from aluminum trialkyls [3, 4].

Thus, at the present time there are rather convenient methods of going from organoaluminum compounds to organoboron compounds. The reverse transition from organoboron compounds to organoaluminum compounds is unknown. Exchange reactions do not take place between organoboron compounds and aluminum halides.

In the present work we have investigated the possibility of a radical exchange reaction between organoboron and organoaluminum compounds.*

The redistribution of radicals between alkyl derivatives of different metals has been rather widely studied through the example of the lithium alkyls, which readily exchange radicals with organic compounds of mercury, antimony, bismuth, lead, magnesium [5], and tin [6], for example:

$$2C_4H_9Li + (C_6H_5)_2Hg \rightleftarrows 2C_6H_5Li + (C_4H_9)_2Hg;$$
$$(C_6H_5)_2Mg + 2C_4H_9Li \rightleftarrows (C_4H_9)_2Mg + 2C_6H_5Li;$$
$$(CH_2{=}CH)_4Sn + 4C_6H_5Li \rightleftarrows CH_2{=}CHLi + (C_6H_5)_4Sn.$$

Sodium alkylis also enter into reactions of a similar type. In a number of cases mercury dialkyls also enter into transalkylation reactions, for example with tetraalkyl derivatives of lead and bismuth [7, 8]. Transalkylation reactions have not been studied for aluminum and boron alkyls. Cases of the exchange of an alkyl for hydrogen between diborane and aluminum trialkyls and alkylmagnesium halides have been described, however [9]:

$$B_2H_6 + 2(C_2H_5)_3Al \longrightarrow 2B(C_2H_5)_3 + 2AlH_3;$$
$$B_2H_6 + 6C_2H_5MgX \longrightarrow 2B(C_2H_5)_3 + 6HMgX.$$

* For a previous communication see Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 181 (1959).

We have studied the exchange of radicals between aluminum and boron trialkyls for the simplest examples. It has been found that heating aluminum triethyl or aluminum trimethyl with boron trialkyls and boron triaryls leads to an exchange of radicals according to the scheme

$$R_3Al + R_3'B \rightleftarrows R_3'Al + R_3B.$$

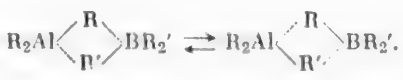
A shift of the equilibrium to the right is achieved because of the fact that the boron trimethyl or boron triethyl that is formed, having a lower boiling point, is distilled off from the reaction mixture as it is formed [b. p. of $(CH_3)_3B$ - 20°, b.p. of $(CH_3)_3Al$ 130°, b.p. of $(C_2H_5)_3B$ 94-95°, b.p. of $(C_2H_5)_3Al$ 190°]. The reaction also is facilitated, apparently, by the circumstance that the mixed boron trialkyls initially formed are easily disproportionated, since it is quite possible to assume that the transalkylation reaction proceeds stepwise through the mixed compounds:

$$R_3Al + R_3'B \rightarrow R_2R'Al + R_2'RB;\ R_2R'Al + R_3'B \rightarrow RR_2'Al + R_2'RB,\ \text{etc.}$$
$$\searrow\ \swarrow$$
$$R_3'B + R_3B$$

The exchange reactions of aluminum triethyl and trimethyl with boron triphenyl, tributyl, and triisobutyl have been studied. The boron triethyl and trimethyl formed in this way were distilled off in the reaction process and the corresponding organoaluminum compound remained in the residue. In a number of experiments, because of the high temperature at which the reaction was carried out, the formation of dialkylaluminum hydride was observed along with the corresponding aluminum trialkyl as a result of the splitting out of olefin from the aluminum trialkyl. The mechanism of the exchange of radicals between organoaluminum and -boron compounds is not yet clear. It may be assumed that the exchange proceeds through the intermediate formation of a complex of the type of aluminum borohydride, such as $R_2AlBR_3'R$, which then breaks down with a new redistribution of radicals

$$R_3Al + R_3'B \rightleftarrows [R_2AlBR_3'R] \rightleftarrows R_2AlR' + R_2'BR.$$

It is possible that the intermediate complex has a bridge structure (as, for example, is now accepted for the structure of the dimer of aluminum trimethyl or triethyl).



In addition to the exchange reactions of organoboron and -aluminum compounds, we have investigated the exchange reactions between aluminum trialkyls and zinc dialkyls, and between boron trialkyls and zinc dialkyls and alkylmagnesium halides. In the case of the aluminum and zinc alkyls the exchange takes place upon heating, and the more volatile organozinc compound gradually distills off from the reaction medium.

$$2R_3Al + 3R_2'Zn \rightarrow 2R_3'Al + 3R_2Zn \uparrow$$

Reactions of aluminum trimethyl with zinc diethyl and zinc dipropyl, and of aluminum triethyl with zinc dibutyl were carried out.

Transalkylation reactions of boron trialkyls with zinc dialkyls were investigated through the example of the reaction of boron triethyl with zinc dimethyl. The more volatile boron trimethyl formed in the reaction distilled off.

$$2(C_2H_5)_3B + 3(CH_3)_2Zn \rightarrow 3(C_2H_5)_2Zn + 2(CH_3)_3B \uparrow$$

The exchange between organoboron and -magnesium compounds was carried out on the example of boron tributyl and ethylmagnesium bromide.

$$3C_2H_5MgBr + (C_4H_9)_3B \rightarrow 3C_4H_9MgBr + (C_2H_5)_3B.$$

The boron triethyl distilled off as it was formed from the reaction medium. By treatment of the residue with carbon dioxide, valeric acid was obtained.

EXPERIMENTAL

Aluminum triethyl and boron triphenyl

In a three-necked flask equipped with a stirrer, an inlet for nitrogen, and a descending condenser were placed 22.8 g of aluminum triethyl and 16.1 g of boron triphenyl. The mixture was gradually heated to 140° with

continuous stirring, and during this process boron triethyl gradually distilled off. After repeated distillation, 6.3 g (96%) of boron triethyl was obtained with b.p. 95-96°, d_4^{20} 0.697. Literature data [5]: b.p. 95°, d^{23} 0.6961. After we had distilled off in vacuum a small amount of aluminum triethyl and a mixture of $(C_2H_5)_2AlC_6H_5$ and $C_2H_5Al(C_6H_5)_2$, which yielded ethane and benzene when decomposed with water, aluminum triphenyl, m.p. 233-235° (from xylene) was obtained by sublimation of the residue in vacuum. Literature data [10]: m.p. 230°, m.p. 237°.

Found %: Al 10.53, 10.72. $(C_6H_5)_3Al$. Calculated %: Al 10.44.

Aluminum trimethyl and boron triphenyl

In a three-necked flask equipped with a stirrer, an inlet for nitrogen, and a descending condenser which had a graduated trap on the outlet, cooled to -70°, were placed 16.1 g of boron triphenyl (0.066 mole) and 7.2 g of aluminum trimethyl (0.1 mole). The mixture was heated to boiling with continuous stirring, and then was heated during the course of 4 hours to 140°. We collected in the trap 3.4 ml of boron trimethyl (60% of theoretical), b.p. -21°, which quickly caught fire in the air; ammoniate, m.p. 56°. Literature data [11]: boron trimethyl, b.p. -21.8°, ammoniate, m.p. 56°. After the intermediate fraction had been distilled off from the residue, aluminum triphenyl was isolated by sublimation, m.p. 233-235°.

Aluminum trimethyl and boron tributyl

In the apparatus used for the study of the reaction between aluminum trimethyl and boron triphenyl were placed 7.2 g of aluminum trimethyl and 18.2 g of boron tributyl (0.1 mole each). While the mixture was boiled vigorously, 4.8 ml (51% of theoretical) of boron trimethyl was collected in the trap, b.p. -20°, ammoniate, m.p. 56°. When the residue was distilled, 6.2 ml of aluminum tributyl was obtained with b.p. 100-105° at 3 mm.

Found: from 0.1616 g of compound 56.9 ml of butane (760 mm, 20°). $(C_4H_9)_3Al$. Calculated: 59.5 ml of butane (760 mm, 20°).

Dibutylaluminum hydride was found in the high-boiling fraction as a contaminant of the aluminum tributyl (decomposition of a sample of the compound yielded a gas containing 8-9% of hydrogen).

Aluminum triethyl and boron tributyl

When a mixture of 36.4 g of boron tributyl and 22.8 g of aluminum triethyl (0.2 mole each) was gradually heated to 200°, 12.2 g (64%) of boron triethyl with b.p. 93-95° was obtained after redistillation. The residue was a mixture of aluminum tributyl and dibutylaluminum hydride, which we did not succeed in separating by distillation. According to any analysis of the gas evolved when a sample of the material was decomposed with water (the gas consisted of butane and hydrogen), the dibutylaluminum hydride content of the various fractions was 60.5-76%.

Aluminum triethyl and boron triisobutyl

Mixing of aluminum triethyl (11.4 g, 0.1 mole) and boron triisobutyl (18.2 g, 0.1 mole) was accompanied by some evolution of heat. When the mixture was gradually heated, about 13 ml of liquid distilled off, from which 4.5 ml of boron triethyl was isolated, and the higher-boiling portion was returned to the reaction. Another 3.1 ml of boron triethyl was obtained, 6.1 g in all (61%). Upon vacuum distillation of the residue only diisobutylaluminum hydride was obtained, with b.p. 115-117° at 1.5 mm.

Found %: H_2 (by decomposition with water) 33. $(iso\text{-}C_4H_9)_2AlH$. Calculated %: H_2 33.3.

Aluminum trimethyl and zinc diethyl

In a three-necked flask equipped with a stirrer, an inlet for nitrogen, and a reflux condenser were placed 28.8 g of zinc diethyl and 16.7 g of aluminum trimethyl (0.232 mole each). The upper end of the reflux condenser was connected with a descending coil condenser; the temperature of the water in the reflux condenser was 50°. When the mixture was heated to 100°, zinc dimethyl began to distil off; the mixture was gradually heated to 140°. Twelve and five-tenths ml of zinc dimethyl were distilled off; after distillation, 13.9 g (62.5%) of zinc dimethyl was obtained:

b.p. 45.5-46.5°, d^{20} 1.380. Literature data [12]: b.p. 46°, $d^{10.5}$ 1.386.

When another 9 ml of zinc diethyl (10.8 g) was added to the residue, 8.4 g more of zinc dimethyl distilled off under the same conditions. By distillation in vacuum of the organoaluminum fraction, 15.5 g (60%) of aluminum

triethyl was obtained with b.p. 86-88° at 3 mm (a sample of the compound on hydrolysis yielded the theoretical amount of ethane). Literature data [13]: b.p. 87-88° at 3 mm.

Aluminum trimethyl and zinc dipropyl

Reaction of aluminum trimethyl (7.2 g, 0.1 mole) with zinc dipropyl (25 g, 0.177 mole) was carried out in a Favorskii flask (with a herringbone dephlegmator 12 cm in height). When the mixture was gradually heated to 140°, 7.3 g (51%) of zinc dimethyl was distilled off with b.p. 45-46°. We did not succeed in isolating pure aluminum tripropyl from the residue by vacuum distillation.

Aluminum triethyl and zinc dibutyl

Transalkylation began at 130-140°, but proceeded at a satisfactory rate only at 160-170°. As a result of such a high reaction temperature, partial decompositon of the organozinc compound took place. From 11.4 g (0.1 mole) of aluminum triethyl and 27 g (0.15 mole) of zinc dibutyl we obtained 10.8 g (58.5%) of zinc diethyl.

By distillation of the residue, 12.0 g of a mixture of aluminum tributyl and dibutylaluminum hydride was obtained (b.p. 119-122° at 5 mm) containing ~50% of the latter (according to analysis of the gas after decomposition with water).

Boron triethyl and zinc dimethyl

In a flask with a reflux condenser connected with a graduated trap (-70°) a mixture of 6.65 g of boron triethyl (0.0665 mole) and 12.7 g of zinc dimethyl (0.133 mole) was heated to boiling. Four and seven-tenths ml of boron trimethyl (2.91 g, 79% of theoretical) was obtained with b.p. -21-(-20°), ammoniate, m.p. 56°.

The zinc diethyl obtained by distillation of the residue apparently contained a slight admixture of boron triethyl (green colored flame).

Ethylmagnesium bromide and boron tributyl

The ether was distilled off from the ethylmagnesium bromide (from 0.2 g of Mg and ethyl bromide), 9.1 g of boron tributyl (0.05 mole) was added to the residue, and the mixture was heated in an atmosphere of nitrogen with a descending condenser to 160° (1.5-2 hours). Four and two-tenths grams (87.5%) of boron triethyl was obtained, b.p. 94.5-96.5°, d^{20} 0.700. Ether was added to the residue and the reaction mass was treated with solid carbon dioxide. n-Valeric acid was obtained, b.p. 185-187°, m.p. 105-106°.

SUMMARY

1. It has been found that when aluminum trialkyls are heated with boron trialkyls a transalkylation reaction occurs. The reaction can be carried to complete exchange of the radicals by removal of the more volatile component from the sphere of reaction.

2. It has been found that a transalkylation reaction takes place between organoaluminum and organozinc compounds.

3. It has been shown that a transalkylation reaction takes place between organoboron and organozinc or organomagnesium compounds.

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*Original Russian pagination. See C. B. translation.

REACTION OF TRIPHENYLALUMINUM WITH TITANIUM HALIDES IN FLUOROBENZENE OR DEUTEROBENZENE SOLUTION

E. V. Mitrofanova, A. N. Artemov, and G. G. Petukhov

Gorkii State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2138-2141, July, 1960
Original article submitted July 18, 1959

Complex catalysts, composed of organic aluminum compounds and titanium halides, are used extensively at the present time for the polymerization of α-olefins. However, the reactions that may take place between these two components have as yet received inadequate elucidation in the literature [1, 2]. This caused us to investigate the reaction of triphenylaluminum with titanium halides in various solvents, both nonpolar—like benzene and cyclohexane, and polar—like fluorobenzene, and determine if the solvent takes part in these processes.

In the previous paper [3] we investigated the reaction of triphenylaluminum with titanium tetrachloride in the inert solvents, benzene and cyclohexane, leading to the formation of biphenyl. It was established that this reaction does not have a free-radical mechanism, since reaction of the phenyl radicals with the solvent—benzene—was not observed here (when the process was run in C^{14}-labeled benzene the isolated biphenyl failed to show any activity).

In this paper we investigated the reaction of triphenylaluminum with titanium tetrachloride and with titanium oxychloride in fluorobenzene. We assumed that a polar solvent could change the mechanism of the reaction of triphenylaluminum with titanium halides. However, also in this solvent both of the above reactions led to the formation of biphenyl. The absence of fluorinated biphenyl derivatives in the reaction products indicated that only the phenyl groups of triphenylaluminum are involved in the formation of biphenyl and that free phenyl radicals are absent in both of the reaction systems. If free phenyl radicals were present it could be expected that they would react with the solvent, which would lead to the formation of mono- and difluorobiphenyls.

As a result, also in a polar solvent like fluorobenzene the reaction of triphenylaluminum with titanium halides does not proceed by a free-radical mechanism. As had been shown in our first paper [3], the biphenyl is probably formed in the decomposition of the initially formed complex.

As had been mentioned, the reaction of triphenylaluminum with titanium tetrachloride in deuterobenzene medium is accompanied by profound H—D exchange, which is caused by compounds with Al—X bonds (X=halide), formed during the reaction process. In support of this is the fact that hydrogen exchange between biphenyl and deuterobenzene goes very easily in the presence of aluminum chloride, whereas such exchange is not observed in the presence of titanium tetrachloride.

In this paper we wanted to establish whether H—D exchange will take place in deuterobenzene medium between triphenylaluminum and other titanium halides, in particular, with titanium oxychloride and titanium trichloride. Here it was interesting to compare the degree of exchange as a function of the taken titanium halides.

With all of the investigated titanium compounds the reaction with triphenylaluminum in deuterobenzene went with the formation of a biphenyl that contained deuterium.

Comparative data on the yield of biphenyl and on its deuterium content for various titanium halides are given in the table. In addition, some dependence of these values on the ratios of the reacting components is shown.

Ratio $AlPh_3$: titanium halide	$TiCl_4$		$TiOCl_2$		$TiCl_3$	
	Yield of biphenyl (%)	Exchange in biphenyl, %	Yield of biphenyl (%)	Exchange in biphenyl, %	Yield of biphenyl (%)	Exchange in biphenyl, %
1 : 1	23.7	65.1	14	8.0	9	19.3
1 : 2	41.8	84.0	21	25.0	13	19.3
1 : 4	25.0	98.0	34	66.0	—	—

Remarks. The amount of C_6D_6 taken was taken 310 mmoles in all experiments. Temperature 15°. Reaction time 48 hr. The yield of biphenyl is given in % on the three phenyl groups of triphenylaluminum.

From the data in the table it can be seen that H−D exchange takes place in all three systems at all of the studied ratios of the reacting components. For tetravalent titanium the degree of exchange increases with increase in the amount of titanium in the reaction mixture. For trivalent titanium ($TiCl_3$) the exchange is more constant and hardly changes with change in the $TiCl_3$ concentration (at a $TiCl_3$: $AlPh_3$ ratio = 11:1 the exchange in biphenyl is 22.0%).

EXPERIMENTAL

All of the experiments were conducted in a nitrogen atmosphere, using nitrogen that had been carefully freed of both moisture and oxygen.

1. Reaction of triphenylaluminum with titanium tetrachloride in fluorobenzene. The triphenylaluminum was obtained by the method of K. A. Kocheshkov and A. N. Nesmeyanov [4], and was identified by the melting point. The fluorobenzene was obtained from aniline by the Schiemann reaction [5], and was analyzed for fluorine [6]. The boiling point of the fluorobenzene was 85.2°.

A charge of 260 mmoles of fluorobenzene, 5.42 mmoles of triphenylaluminum and 8.37 mmoles of titanium tetrachloride was placed in a tightly fitting ground-glass stoppered flask through which a constant stream of nitrogen was passed. The $TiCl_4$: $AlPh_3$ ratio was 1.5:1. Then the flask was closed tightly and shaken. A solid reddish-brown complex formed immediately. The reaction mixture was allowed to stand for 48 hr at 15° with periodic shaking. Since it had been established earlier [3] by several methods that the biphenyl is formed as the primary reaction product, and not as the result of hydrolysis of the reaction mixture, then in this and all subsequent experiments we used the simplest method to isolate the reaction products, namely, decomposition of the reaction mixture with water and subsequent steam distillation of the fluorobenzene and other reaction products. It should be mentioned that during the steam distillation the water solutions acquired the blue-violet color characteristic of trivalent titanium salts, which persisted throughout the entire distillation. This phenomenon was observed in all of the reactions of $AlPh_3$ with titanium halides.

After steam distillation the fluorobenzene was separated from the water, dried over calcium chloride, and distilled. A product was isolated from the residue that proved to be biphenyl. It had m.p. 70° after recrystallization from ethanol. The biphenyl was analyzed for fluorine [6], since it could contain traces of mono-and difluorobiphenyl as impurity. Analysis revealed that fluorine was absent in the compound. The yield of biphenyl based on the three phenyl groups of triphenylaluminum was 30%.

2. Reaction of triphenylaluminum with titanium oxychloride in fluorobenzene. The titanium oxychloride was obtained by the method described in [7]. The reaction was run under conditions similar to those described above. For reaction we took 260 mmoles of fluorobenzene, 6.05 mmoles of triphenylaluminum and 6.89 mmoles of titanium oxychloride. The $TiOCl_2$: $AlPh_3$ ratio was 1.15:1. Biphenyl was isolated from the reaction products, which after recrystallization from ethanol had m.p. 69−70°, and by analysis was shown to be free of fluorine. The yield of biphenyl, based on the three phenyl groups of triphenylaluminum, was 25%.

It should be mentioned that we ran an experiment showing that triphenylaluminum does not react with fluorobenzene, before running the experiments in fluorobenzene. The triphenylaluminum was isolated from the fluorobenzene solution as its derivative with benzalacetophenone, namely, as 1, 1-diphenylpropiophenone. In order to establish that the phenyl groups did not contain fluorine, since it was possible for exchange processes to take place in the system, the 1,1-diphenylpropiophenone was analyzed for fluorine. The analysis gave a negative result.

3. Reaction of triphenylaluminum with titanium trichloride in deuterobenzene. The titanium trichloride was obtained by the method given above. The work-up was followed by the exchange of benzene with deuterosulfuric acid. The reaction vessel was a flask equipped with a well fitting ground-glass stopper. With a constant stream of nitrogen blowing through the flask, the charge of deuterobenzene, triphenylaluminum and titanium halide was loaded into the flask. Then the flask was stoppered tightly and the contents were mixed. A solid brown complex formed immediately. The reaction mixture was allowed to stand for 48 hr at 15° with periodic shaking. After this the contents were poured into water, and the mixture of deuterobenzene and dissolved biphenyl was removed by steam distillation. The benzene layer was separated from the water layer, dried over calcium chloride, and fractionally distilled. After distilling off the deuterobenzene, we isolated biphenyl from the residue which was identified by the melting point. M.p. 69-70° (from ethanol), which was not depressed when the compound was mixed with pure biphenyl.

SUMMARY

1. In a polar solvent like fluorobenzene the reaction of triphenylaluminum with the titanium halides $TiCl_4$ and $TiOCl_2$ goes without the formation of free radicals. The reaction product is biphenyl, which is formed in the decomposition of the original complex. The solvent does not take part in the reaction.

2. The titanium halides $TiCl_4$, $TiOCl_2$ and $TiCl_3$ react with triphenylaluminum in deuterobenzene solution to form deuterated biphenyl, which is formed as the result of H–D exchange between the biphenyl and the deuterobenzene. Tetravalent titanium compounds catalyze the H–D exchange.

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AROMATIC HYDROCARBONS

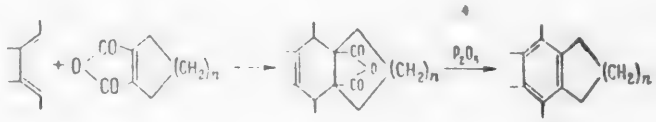
XV. PINACOLS IN THE DIENE SYNTHESIS

V. R. Skvarchenko, Ling Wèeng-lien, and R. Ya. Levina

Moscow State University

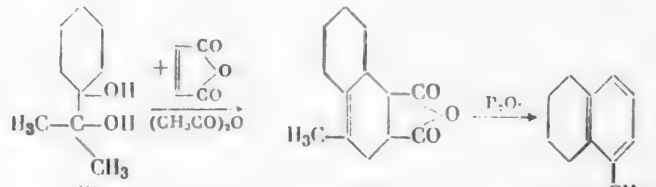
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2141 - 2145, July, 1960
Original article submitted July 10, 1959

In previous papers we described a new method for the synthesis of tetralins [1, 2] and indans [3], consisting in the aromatization of adducts of dienic hydrocarbons with cyclic analogs of maleic anhydride under the influence of phosphorus pentoxide.



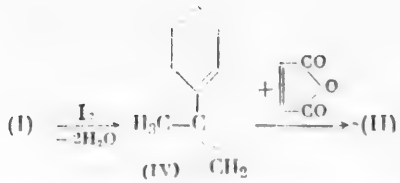
$n = 1, 2.$

In this paper we describe the preparation of several hydrocarbons belonging to these two classes of compounds, and specifically, the synthesis of 5-methyltetralin, 5,8-dimethyltetralin, and 4-methylindan; the syntheses were accomplished by treating the anhydrides of the appropriate Δ^4-cycloalkenyl-1,2-dicarboxylic acids with phosphorus pentoxide. However, in contrast to those described earlier, the anhydrides used in this study were obtained from the simpler components of the diene synthesis—from the reaction of the pinacols of cyclic ketones with either maleic or methylmaleic anhydride (the latter taken in excess). Thus, 5-methyltetralin (III) was obtained (in 50% yield) by treating the anhydride of 4-methyl-Δ^4-octalin-1,2-dicarboxylic acid (II) with phosphorus pentoxide; this anhydride was obtained (in 54% yield) by heating pinacol (I) (from acetone and cyclohexanone) with excess maleic anhydride for 15 min in acetic anhydride.

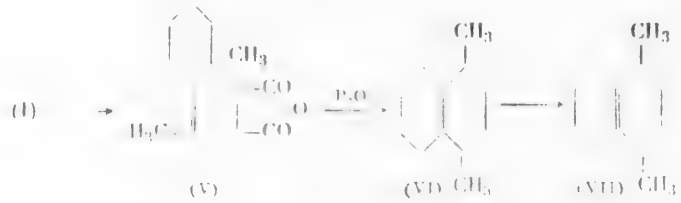


(I) (II) (III)

The anhydride of 4-methyl-Δ^4-octalin-1,2-dicarboxylic acid (II) was also obtained by the counter synthesis—directly from 1-isopropenylcyclohexene and maleic anhydride by heating in xylene; in this case the yield of the adduct was 40%, based on the starting 1-isopropenylcyclohexene (IV). However, this diene in turn was obtained in 40% yield from pinacol (I) by refluxing with iodine. As a result, the yield of anhydride (II) in this case, based on pinacol (I), was only 23%.



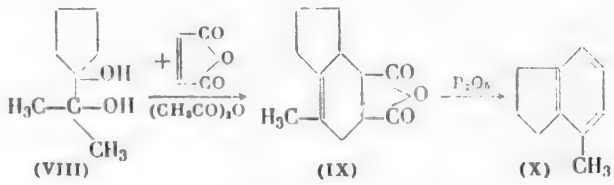
To obtain 5,8-dimethyltetralin (VI, yield 62%) we decomposed the anhydride of 1,4-dimethyl-Δ^4-octalin-1,2-dicarboxylic acid (V), obtained in turn (in 47% yield) from pinacol (I) and methylmaleic anhydride by refluxing in acetic anhydride for 30 min, by heating with phosphorus pentoxide.



5,8-Dimethyltetralin (VI) was then converted by heating with sulfur to 1,4-dimethylnaphthalene (VII), which was identified by the melting point of its picrate and also by the infrared absorption spectrum (λ_{max} 277, 287, 300, 316; $\log\epsilon_{max}$ 3.83, 3.85, 3.62, 2.68).

Apparently, the 5,8-dimethyltetralin and 1,4-dimethylnaphthalene obtained by us were not contaminated with the isomeric hydrocarbons—5,7-dimethyltetralin and 1,3-dimethylnaphthalene, respectively—the formation of which could occur if the starting anhydride (V) contained a small amount of the isomeric "meta" adduct—the anhydride of 2,4-dimethyl-Δ^4-octalin-1,2-dicarboxylic acid—as impurity.

4-Methylindan (X) was obtained (yield 48%) by heating the anhydride of 4-methyl-5,6-cyclopentano-Δ^4-cyclohexene-1,2-dicarboxylic acid (IX), the reaction product of maleic anydride with the pinacol (VIII) obtained from acetone and cyclopentanone (yield 35%), with phosphorus pentoxide.



The use of pinacols as the dienic component when running the reaction with either maleic or methylmaleic anhydride (in acetic anhydride) makes it possible to eliminate the stage of preparing the dienic hydrocarbons (dehydration of the pinacols), which compounds are frequently quite unstable and polymerize with ease under the conditions of the diene synthesis; using either maleic or methylmaleic anhydride as the dienophile makes it possible to regard the described method of preparing 5-methyltetralin, 5,8-dimethyltetralin and 4-methylindan as being simpler than the method developed by us earlier, in which the anhydrides of cyclohexene- and cyclopentenedicarboxylic acids (the synthesis of which is quite complicated) were used as the dienophiles.

EXPERIMENTAL

Pinacol (I) was obtained by the method described in [4], by the reduction of a mixture of equimolar amounts of cyclohexanone and acetone in benzene solution using aluminum amalgam. M.p. 81–82° (literature: m.p. 82–83°).

1-Isopropenylcyclohexene (IV) was obtained by the dehydration of pinacol (I) (20 g), by heating (on the water bath) with iodine (0.5 g); the hydrocarbon was vacuum-distilled immediately; b.p. 65–67° (20 mm), n_D^{20} 1.4975, yield 6 g (40%). Literature data [5]: boiling point 66–68° (20 mm), n_D^{25} 1.4978.

The anhydride of 4-methyl-Δ^4-octalin-1,2-dicarboxylic acid (II) was obtained by heating pinacol (I) (20 g) with maleic anhydride (80 g) in acetic anhydride (250 ml) for 15 min, in the presence of hydroquinone (0.1 g) and using a stream of nitrogen. The next day the reaction mixture was vacuum-distilled; adduct (II) (15 g, 54% yield) with b.p. 150-180° (10 mm) was isolated, which crystallized on standing and after recrystallization from petroleum ether had m.p. 74-75°. Literature data [5]: m.p. 76.2°.

Anhydride (II) was also obtained by the reaction of maleic anhydride with 1-isopropenylcyclohexene (IV), by heating in either xylene [5] or propionic acid. The mixture of the anhydrides, obtained from the pinacol and from 1-isopropenylcyclohexene, melted without depression.

5-Methyltetralin (III). A mixture of 18.2 g of anhydride (II) and 12.8 g of phosphorus pentoxide was gradually heated in a metal bath from 160 to 300° until carbon monoxide was no longer evolved; the obtained hydrocarbon was distilled from the reaction mixture, after which it was washed with 10% sulfuric acid (to remove any possible starting anhydride), then with water, dried over calcium chloride, and finally it was redistilled in vacuo over metallic sodium (yield 6.5 g or 50%).

Boiling point 75° (5 mm), n_D^{20} 1.5470, d_4^{20} 0.9699, MR_D 47.8. $C_{11}H_{14}F_3$. Calculated 47.20.

Literature [6]: Boiling point 234.35° (760 mm), 147.76° (57.3 mm), n_D^{20} 1.54395, d_4^{20} 0.9720.

The dehydrogenation of 5-methyltetralin (1.8 g) was accomplished by heating with sulfur (0.8 g) in a metal bath at 220–240° for 4 hr; the 1-methylnaphthalene was distilled from the reaction mixture and than it was redistilled over metallic sodium (yield 0.92 g, 54%).

B.p. 148–149° (57 mm); picrate, m.p. 141° (from alcohol).

Literature [7]: 1-methylnaphthalene, b.p. 151.3° (58 mm), 244.78° (760 mm); picrate, m.p. 141–142°.

The anhydride of 1,4-dimethyl -Δ^4-octalin-1,2-dicarboxylic acid (V) was obtained by heating pinacol (I) (31.6 g) with excess methylmaleic anhydride (67 g) for 30 min, in a stream of nitrogen, in acetic anhydride (300 ml) in the presence of hydroquinone (0.1 g). Vacuum-distillation of the reaction mixture led to the isolation of adduct (V) (22 g, 47%; not described in the literature) with b.p. 156–158° (8 mm), which crystallized on standing and had m.p. 102° (from a mixture of acetone and petroleum ether).

Found %: C 71.64, 71.58; H 7.47, 7.65. $C_{14}H_{18}O_3$. Calculated %: C 71.76; H 7.74.

5,8-Dimethyltetralin (VI) was obtained by the gradual heating of a mixture of 17.5 g of anhydride (V) and 12 g of phosphorus pentoxide from 210 to 290°; the obtained hydrocarbon was removed from the reaction mixture by vacuum-distillation, after which it was heated with 25% caustic solution, then extracted with ether, washed with water, dried over calcium chloride, and then distilled from sodium (yield 7.5 g, 62%).

B.p. 250–251° (748 mm), 129–130° (19.5 mm), n^{20}_D 1.5475, d^{20}_4 0.9694, MR_D 52.44. $C_{12}H_{16}F_3$. Calculated 51.82.

Literature data: 5,8-dimethyltetralin [8], b.p. 254° (760 mm), 121° (1 mm); 5,7-dimethyltetralin [9], b.p. 250–252° (760 mm), n^{20}_D 1.5409, d^{21}_4 0.9589.

The dehydrogenation of 5,8-dimethyltetralin was run in the same manner as the dehydrogenation of 5-methyltetralin. The isolated 1,4-dimethylnaphthalene (VII) had the following constants:

b.p. 130–131° (14 mm), n^{20}_D 1.6100, d^{20}_4 1.0130, MR_D 53.56. $C_{12}H_{12}F_5$. Calculated 50.88, m.p. 142–143°.

Literature data [10]: 1,4-dimethylnaphthalene, b.p. 263° (760 mm), n_D^{20} 1.6127; picrate, m.p. 143°; 1,3-dimethylnaphthalene, b.p. 263° (760 mm), n_D^{20} 1.6078; picrate, m.p. 116.5°.

Pinacol (VIII) (from cyclopentanone and acetone) was obtained in the same manner as pinacol (II) [4]; m.p. 64° (literature data: m.p. 64–65°).

The anhydride of 4-methyl-5,6-cyclopentano-Δ^4-cyclohexene-1,2-dicarboxylic acid (IX) (not described in the literature) was obtained from 20 g of pinacol (VIII) and 80 g of maleic anhydride by the same procedure as was used to obtain anhydride (II).

B.p. 150–180° (15 mm) m. p. 58–59° (from petroleum ether), yield 10 g (35%).

Found %: C 69.64, 69.41; H 6.75, 7.03. $C_{12}H_{14}O_3$. Calculated %: C 69.88; H 6.84.

4-Methylindan (X). A mixture of 13 g of anhydride (IX) and 8.5 g of phosphorus pentoxide was heated gradually from 210 to 250° (in a metal bath) until the evolution of carbon monoxide ceased; the obtained hydrocarbon was removed by distillation, dissolved in petroleum ether, refluxed for 1 hr with 20% NaOH solution, washed with water, and dried over calcium chloride. Then the petroleum ether was removed by distillation and the residue was vacuum-distilled from sodium; we isolated 4 g (48%) of product.

B.p. 101–103° (32 mm), n^{20}_D 1.5324, d^{20}_4 0.9564, MR_D 42.85. $C_{10}H_{12}F_3$. Calculated 42.59.

5,6,7-Tribromo-4-methylindan (obtained by the bromination of 4-methylindan in the presence of a trace of iodine) had m.p. 183–183.5° (from a mixture of alcohol and toluene).

Literature data: 4-methylindan, b.p. 84–85° (20 mm), n^{20}_D 1.5323, d^{20}_{20} 0.956 [11]; tribromide, m.p. 183° [12].

SUMMARY

1. We were the first to react the mixed pinacols (as the diene component) from acetone and cyclic ketones (cyclohexanone and cyclopentanone) with maleic and methylmaleic anhydrides. When these pinacols were heated with excess maleic anhydride in acetic anhydride we obtained in turn the anhydrides of 4-methyl-Δ^4-octalin-1,2-dicarboxylic, 1,4-dimethyl-Δ^4-octalin-1,2-dicarboxylic and 4-methyl-5,6-cyclopentano-Δ^4-cyclohexene-1,2-dicarboxylic acids.

2. The synthesized anhydrides were converted by heating with phosphorus pentoxide to 5-methyltetralin, 5,8-dimethyltetralin and 4-methylindan, respectively.

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*Original Russian pagination. See C. B. translation.

SYNTHESIS OF HYDROCARBONS

LXXV. NEW SYNTHESIS OF 1,1,3,3-TETRAALKYLCYCLOHEXANES

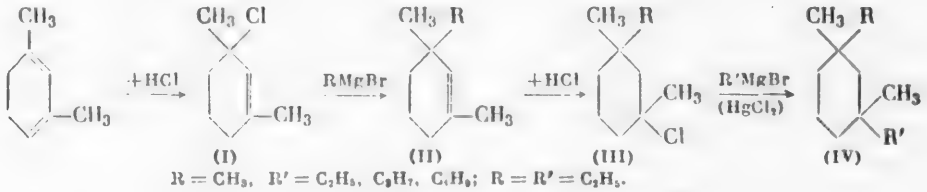
R. Ya. Levina, V. K. Daukshas, and T. P. Surikova

Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2145-2148, July, 1960
Original article submitted July 10, 1959

Cyclohexane hydrocarbons, containing two quaternary carbon atoms in the ring, were first described in [1]. Only a few hydrocarbons of this type have been synthesized up to now, which is explained by the absence of general and sufficiently simple methods for their synthesis. At the same time, cyclohexane hydrocarbons with quaternary carbon atoms in the ring are present in petroleum distillates [2], and in order to identify them it is necessary to have pure cyclohexane hydrocarbons of rigidly established structure as standards.

The purpose of the present study was to develop a general method for the synthesis of 1,1,3,3-tetraalkylcyclohexanes, i.e., for the synthesis of cyclohexane hydrocarbons containing two quaternary carbon atoms, separated by a methylene group, in the ring. The synthesis of these hydrocarbons was accomplished in accordance with the following scheme.



R = CH_3, R' = C_2H_5, C_3H_7, C_4H_9; R = R' = C_2H_5.

The trialkylcyclohexenes (II), the synthesis of which from dimethylcyclohexadiene was described by one of us earlier [3]*, were subjected to hydrochlorination and the obtained saturated tertiary chlorides (III) were then introduced into the Grignard–Wurtz reaction in the presence of mercuric chloride. When reacted with alkylmagnesium bromides, the chlorides (III) not only exchanged the chlorine atom for the alkylmagnesium bromide radical, but they also cleaved hydrogen chloride, forming the original trialkylcyclohexenes (II) in about 75% yield. The latter were easily separated from the end reaction products, the tetraalkylcyclohexanes (IV) (yield 28–60%, based on consumed trialkylcyclohexene), by distillation and could be recycled.

As can be seen from the equation given above for the reaction, the method developed by us can also be used to synthesize those 1,1,3,3-tetraalkylcyclohexanes where only two of the four alkyl groups are methyls, since the latter are already present in the molecule of the starting dimethylcyclohexadiene. In [1] the starting substance for the synthesis of 1,1,3,3-tetraalkylcyclohexanes was trimethylcyclohexenone (isophorone), which permitted the authors to synthesize only 1,1,3-trimethyl-3-alkylcyclohexanes.

* When the hydrochloride of the dimethylcyclohexadiene is used in place of the earlier used [3] hydrobromide the yield of the trialkylcyclohexenes increases from 13–27 to 35–40%, based on the starting diene. It was shown earlier [3] that these compounds are not contaminated by the isomeric trialkylcyclohexenes, with a different arrangement of the alkyl groups.

1,1,3,3-Tetraalkylcyclohexanes

Name	Freezing point	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	ν_{20} centistokes	Found** (%) C	Found** (%) H	Empirical formula	Yield (%)
1,1,3-Trimethyl-3-ethylcyclohexane•a	−100° (glass)	179–180° (743)	1.4472	0.8113	50.32	50.80	2.00	85.40, 85.49	14.60, 14.47	$C_{11}H_{22}$	15
1,1,3-Trimethyl-3-propylcyclohexane•b	−95 (glass)	194–194.5 (740)	1.4493	0.8155	55.44	55.42	2.16	85.59, 85.67	14.42, 14.33	$C_{12}H_{24}$	8
1,1,3-Trimethyl-3-butylcyclohexane	−80 (glass)	217–218 (731)	1.4522	0.8171	60.21	60.03	3.16	85.58, 85.76	14.46, 14.39	$C_{13}H_{26}$	7
1,3-Dimethyl-1,3-diethylcyclohexane	−100 (glass	88.9–89.2 (9)	1.4561	0.8267	55.39	55.42	2.51	85.67, 85.52	14.50, 14.60	$C_{12}H_{24}$	15

•Literature data [1]: a) b.p. 180.9–181.5° (760 mm), n_D^{20} 1.4473, d_4^{20} 0.8132; b) b.p. 202.3–202.5° (760 mm), n_D^{20} 1.4488, d_4^{20} 0.8154. The other hydrocarbons are new.

••Calculated %: C 85.64; H 14.36

As a result, the synthesis method developed by us offers greater possibilities in the sense that the quaternary carbon atoms in the synthesized 1,1,3,3-tetraalkylcyclohexanes can be linked to a large number of alkyl groups, differing both in the number of carbon atoms and in the carbon skeleton.

With the described method we synthesized some 1,1,3-trimethyl-3-alkylcyclohexanes, and also 1,3-dimethyl-1,3-diethylcyclohexane. This last hydrocarbon (IV; R = R' = C_2H_5) can exist in the form of the cis- and trans-isomers; an attempt was made to separate these isomers by fractional distillation of the obtained hydrocarbon in vacuo through a highly efficient column (80 theoretical plates). However, the presence of the two stereoisomers could not be shown by distillation, since the synthesized 1,3-dimethyl-1,3-diethylcyclohexane boiled within a range of 0.3°, and the separately collected narrow fractions proved to have completely identical constants.

EXPERIMENTAL

Synthesis of trialkylcyclohexanes (II). Using a mixture of ice and salt for cooling, a stream of dry hydrogen chloride was passed into 108 g (1 mole) of 1,3-dimethyl-1,3-cyclohexadiene (synthesized as described in [3] by reacting 1-methyl-1-cyclohexen-3-one with methylmagnesium bromide; yield 65%; b.p. 135-136° at 750 mm, n_4^{20} 1.4813, d_4^{20} 0.8328) till the increase in weight was 37 g. The thus-obtained dimethylcyclohexadiene monohydrochloride, 1-chloro-1,3-dimethyl-2-cyclohexene (I), cleaves hydrogen chloride with unusual ease; for this reason immediately after preparation (without distilling) it was diluted with ether (1 : 1) and then reacted with the alkylmagnesium bromides (36 g of Mg, 1.6 moles of alkyl bromide and 300 ml of ether), by adding in drops, with ice water cooling. The next day the reaction mixture was refluxed for 3 hr, after which it was decomposed by pouring over ice containing some acetic acid. After conventional treatment, the yield of the trialkylcyclohexenes (II) was 35-40%, based on the starting dimethylcyclohexadiene.

1,1,3-Trimethyl-2-cyclohexene, b.p. 138-138.5° (750 mm), n_D^{20} 1.4580, d_4^{20} 0.8110. 1,3-Dimethyl-1-ethyl-2-cyclohexene, b.p. 50-52° (10 mm), n_D^{20} 1.4589, d_4^{20} 0.8224.

Literature data, respectively [3]: b.p. 137.5-138.8° (757 mm) n_D^{20} 1.4583, d_4^{20} 0.8123; b.p. 164-164.4° (757 mm), n_D^{20} 1.4593, d_4^{20} 0.8278.

Synthesis of tetraalkylcyclohexanes (IV). The trialkylcyclohexenes (II) were shaken for 2 to 3 days with concentrated hydrochloric acid that had been saturated in the cold with hydrogen chloride. The obtained saturated

tertiary chlorides (III) were washed with water and then dried. Four grams of mercuric chloride was added to an ether solution of the alkylmagnesium bromide (24 g of Mg, 1.1 moles of alkyl bromide and 200 ml of ether) and after it had dissolved the distilled tertiary chloride (III), obtained from 0.5 mole of the trialkylcyclohexene (II), was added in drops at 12–15°. The next day the reaction mixture was refluxed for 3 hr and then it was decomposed with 2N hydrochloric acid; the ether layer was separated, washed with water, than with 2N sodium carbonate solution, and finally it was dried. After distilling off the ether the residue was refluxed for 30 min over sodium, and then it was distilled. The fractions collected were the starting trialkylcyclohexene (II) (the amount recovered from the reaction was approximately 75%) and the much higher boiling tetraalkylcyclohexane (IV). The latter was shaken for 30 min with hot concd hydrochloric acid (to remove any organomercury compounds), washed with water, then with 2N sodium carbonate solution, dried, distilled from sodium, and finally it was fractionated through a column having an efficiency of 35 theoretical plates. The obtained tetraalkylcyclohexanes (IV) were purified further by chromatographing on silica gel The yield was 7–15%, based on trialkylcyclohexene taken for reaction, or 28–60%, based on amount of trialkylcyclohexene consumed in the reaction; the constants and the analysis data for the synthesized hydrocarbons are given in the table The Raman spectra of the synthesized tetraalkylcyclohexanes failed to show frequencies in the 1600–1680 cm^{-1} region, which indicated the absence of unsaturated hydrocarbons as impurity

SUMMARY

1. Starting with 1,3-dimethyl-1,3-cyclohexadiene, a general method was developed for the synthesis of cyclohexane hydrocarbons containing two quaternary carbon atoms, separated by a methylene group, in the ring. Specifically, these compounds are 1,1,3,3-tetraalkylcyclohexanes.

1. The 1,1,3-trimethyl-3-ethyl, 1,1,3-trimethyl-3-propyl-1,1,3-trimethyl-3-butyl- and 1,3-dimethyl-1,3--diethylcyclohexanes were synthesized using this procedure.

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*Original Russian pagination. See C. B. translation.

SYNTHESIS OF BRANCHED $C_{12} - C_{16}$ ACIDS IN THE $C_nH_{2n+1}COOH$ SERIES

G. I. Nikishin, Yu. N. Ogibin, and A. D. Petrov

Institute of Organic Chemistry, Academy of Sciences of the USSR

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2148-2153, July, 1960
Original article submitted June 29, 1959

Synthetic straight-chain acids, replacing fats in the production of soap, are obtained by the oxidation of paraffin with atmospheric oxygen. The production of branched acids on a commercial scale has not been accomplished yet, although researches are already in progress in which the objective is to find simple and easily executed methods for the synthesis of such acids. At the present time the most promising methods for the synthesis of branched acids on an industrial scale are the oxidation of isoparaffins and the carboxylation of olefins with carbon monoxide and water in the presence of sulfuric acid [1]. The surface-active properties of the branched acids have as yet received very little study. Included in the investigations on the matter is a paper in which only the surface tension of solutions of the salts of dialkylacetic acids were determined [2].

The present paper is devoted to the synthesis of the individual branched carboxylic acids of composition $C_{12}-C_{16}$ by the organomagnesium method, for the purpose of making a later study of the surface-active properties and detergent action of their sodium salt solutions. The synthesis of the acids was accomplished in accordance with the following scheme:

$$CH_2{=}CH{-}CH{=}CH{-}CH_3 \xrightarrow{HCl} CH_3{-}CHCl{-}CH{=}CH{-}CH_3 \xrightarrow{RMgBr}$$
$$\longrightarrow R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH{-}CH_3 \xrightarrow{HBr} R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CHBr}} \xrightarrow[2.\ HCl\text{-}acid]{1.\ Mg+CO_2}$$
$$\longrightarrow R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH$$

Together with the acids, hydrocarbons are formed in the last step of the synthesis due to condensation of two molecules of the alkyl bromide by the Grignard–Wurtz reaction.

$$2R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CHBr}} + Mg \longrightarrow R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}R + MgBr_2$$

Replacing the magnesium by lithium causes the yield of the hydrocarbons to increase and that of the acids to decrease.

From 2-chloro-3-pentene (prepared by reacting concd. hydrochloric acid with piperylene [3]) and alkylmagnesium bromides we prepared a number of β-olefins, the properties and structures of which are given in Table 1. The yields of the β-olefins obtained from primary alkylmagnesium bromides ranged from 50 to 60% (based on the Grignard reagent), while in the case of the secondary and tertiary alkylmagnesium halides the yields of the olefins were lower. The synthesis of β-olefins from 2-chloromagnesium-3-pentene and alkyl bromides could not be ac-

TABLE 1. β-Olefins, R–CH(CH_3)–CH=CH–CH_3

R	Ratio RBr : Mg : 2-chloro-3-pentene	Yield (in %) on:		Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Found (%)		Empirical formula	Calculated (%)	
		RMgBr	Olefin				found	calculated	C	H		C	H
n-C_6H_{13}	1.0 : 1.3 : 1.25	93	73	68.5—69.5° (12)	1.4278	0.7496	52.93	52.71	—	—	$C_{11}H_{22}$	—	—
n-C_7H_{15}	1.0 : 1.25 : 1.20	93	68.5	197—198 80—81 (10)	1.4319	0.7578	57.60	57.35	85.80, 85.90	14.23, 14.34	$C_{12}H_{24}$	85.63	14.37
n-C_8H_{17}	1.0 : 1.3 : 1.4	99	60.3	219—220 103—105 (12)	1.4351	0.7645	62.27	62.00	85.40, 85.63	14.35, 14.36	$C_{13}H_{26}$	85.63	14.37
n-C_9H_{19}	1.0 : 1.25 : 1.2	96	57.3	240—242 109—110 (7)	1.4380	0.7708	66.88	66.65	85.65, 85.56	14.38, 14.37	$C_{14}H_{28}$	85.63	14.37
n-$C_{10}H_{21}$	1.0 : 1.25 : 1.2	92	63.8	252—255 138—140 (13)	1.4413	0.7758	71.65	71.30	85.60, 85.55	14.20, 14.20	$C_{15}H_{30}$	85.63	14.37
n-$C_6H_{13}(CH_3)CH$	1.0 : 1.5 : 1.25	83.7	40	87—88 (9)	1.4387	0.7740	61.92	62.00	85.44, 85.41	14.33, 14.42	$C_{13}H_{26}$	85.63	14.37
n-$C_4H_9CH(C_2H_5)CH_2$	1 : 1.25 : 1.5	81.2	53.5	205—207 90 (10)	1.4361	0.7705	61.81	62.00	85.80, 85.77	14.20, 14.41	$C_{13}H_{26}$	85.63	14.37
$(CH_3)_3C$*	1 : 1.4 : 1.0	78	14	79.5 (140)	1.4221	0.7397	43.37	43.41	—	—	C_9H_{18}	—	—
p-$CH_3C_6H_{10}$	1.0 : 1.25 : 1.25	90	45.3	80 (9)	1.4622	0.8301	55.10	55.30	86.40, 86.45	13.28, 13.51	$C_{12}H_{22}$	86.66	13.34
C_6H_5	1.0 : 1.25 : 1.25	99	78	82—82.5 (16)	1.5093	0.8837	49.42	49.21	90.35, 90.22	9.74, 9.79	$C_{11}H_{14}$	90.35	9.65

* B.p. 128—129°, n_D^{25} 1.4198, d_4^{25} 0.7382 [4].

complished with satisfactory yields under the conditions adopted by us (mole ratio magnesium: 2-chloro-3-pentene = 1.25 : 1, 600 ml of ether, 35°). Here the predominant reaction was the condensation of two molecules of 2-chloro-3-pentene to 4,5-dimethyl-2,6-octadiene [4]. The 2-alkyl-3-pentenes of lower molecular weight were synthesized earlier by a similar scheme, with the difference that 2-bromo-3-pentene, prepared from the corresponding unsaturated alcohol, served as the starting material; in this connection the β-olefins were obtained in smaller yields [4].

TABLE 2. Alkyl Bromides, R–CH(CH_3)–CH_2–CH(CH_3)Br

R	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Empirical formula
n-C_6H_{13}	76° (2)	1.4589	1.0561	60.87	60.90	$C_{11}H_{23}Br$
n-C_7H_{15}	87.5—89 (1)	1.4604	1.0434	65.47	65.54	$C_{12}H_{25}Br$
n-C_8H_{17}	95—97 (1)	1.4615	1.0319	70.07	70.19	$C_{13}H_{27}Br$
n-C_9H_{19}	103—104 (1)	1.4622	1.0203	74.74	74.84	$C_{14}H_{29}Br$
n-$C_{10}H_{21}$	115.5—116 (1)	1.4628	1.0094	79.42	79.49	$C_{15}H_{31}Br$
n-$C_6H_{13}CH(CH_3)CH_2$	79—80 (1)	1.4650	1.0393	70.03	70.19	$C_{13}H_{27}Br$
n-$C_4H_9CH(C_2H_5)CH_2$	96—98 (1)	1.4652	1.0405	69.95	70.19	$C_{13}H_{27}Br$

A number of 2-alkyl-4-bromopentanes (Table 2) were obtained by the reaction of 2-alkyl-3-pentenes with HBr. To prove the order in which the hydrogen bromide added to the olefins we synthesized 2-methyl-4-bromopentane by two procedures:

$$CH_3–CH=CH–CHCl–CH_3 + CH_3MgCl \longrightarrow CH_3–CH=CH–CH(CH_3)_2 \xrightarrow{HBr} CH_3–CHBr–CH_2–CH(CH_3)_2 \quad (1)$$

$$CH_3–CHO + (CH_3)_2CHCH_2Cl + Mg \longrightarrow CH_3–CHOH–CH_2–CH(CH_3)_2 \xrightarrow{HBr} CH_3–CHBr–CH_2–CH(CH_3)_2. \quad (2)$$

Both bromides had the same physicochemical constants and the same Raman spectrum, which confirms the validity of the indicated order of HBr addition.

The synthesis of carboxylic acids from haloalkanes by the Grignard reaction was accomplished earlier on a small number of examples. Only low-molecular acids were obtained using the method. The synthesis of isobutyric acid from isopropyl bromide and carbon dioxide was accomplished in 90% yield [5], while isovaleric acid was obtained from sec-butyl bromide in 66% yield [6]; the yield of the same acid from the corresponding chloride was 80% [7]. The higher molecular-weight acids, methylneopentylacetic [8] and methylhexylacetic [9], were also synthesized by a similar procedure.

In this paper we synthesized those acids having either two or three side-chains in the main aliphatic chain. The ratios of the taken reactants as well as the properties and yields of the obtained acids are given in Table 3. These acids are either colorless or slightly yellow liquids, odorless, and congealing to a glass at -60 to -70°. The structures of the hydrocarbons formed in the synthesis of the acids and their properties and yields are given in Table 4. The difference between the calculated (using the bond refractions) and the found molecular refractions for the hydrocarbons, where R is a normal aliphatic radical of composition $C_6–C_{10}$, is 0.7–0.8. This difference drops to 0.03–0.08 when the bond subtypes [10] are taken into consideration in calculating the MR_D; for branched radicals the difference is 0.1–0.2.

EXPERIMENTAL

The β-olefins (Table 1), alkyl bromides (Table 2) and the acids (Table 3) were obtained employing the same method for each separate class of compounds. We will describe in detail only the typical synthesis of 2,4-dimethylundecanoic acid.

TABLE 3. Acids, R–CH(CH$_3$)CH$_2$CH(CH$_3$)–COOH

R	Yield (in %)		Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Found (%)		Empirical formula	Calculated (%)	
	R'MgBr*	acid				found	calculated	C	H		C	H
n -C_6H_{13}	45	100	113—114° (1)	1.4420	0.8896	59.57	59.40	71.86, 72.07	12.05, 12.14	$C_{12}H_{24}O_2$	71.95	12.08
n -C_7H_{15}	50.5	76.3	141.5—143 (4)	1.4440	0.8884	64.08	64.05	72.66, 72.64	12.00, 11.98	$C_{13}H_{26}O_2$	72.84	12.23
n -C_8H_{17} **	40.15	55	148—150 (2)	1.4456	0.8869	68.61	68.70	73.78, 73.71	12.18, 12.31	$C_{14}H_{28}O_2$	73.63	12.35
n -C_9H_{19}	60.3	52.0	162—164 (2)	1.4470	0.8857	73.13	73.34	74.42, 74.56	12.58, 12.53	$C_{15}H_{30}O_2$	74.32	12.48
n -$C_{10}H_{21}$	38.3	49.08	144—145 (0.5)	1.4487	0.8843	77.72	77.99	75.00, 75.00	12.50, 12.51	$C_{16}H_{32}O_2$	74.94	12.58
n $C_6H_{13}(CH)_3CH$	50	75	120 (0.5)	1.4490	0.8932	68.60	68.70	73.91, 74.14	12.40, 12.37	$C_{14}H_{28}O_2$	73.63	12.36
n -$C_4H_9CH(C_2H_5)CH_2$	51.3	78	115—116 (0.5)	1.4491	0.8914	68.74	68.70	74.10, 73.87	12.35, 12.36	$C_{14}H_{28}O_2$	73.63	12.36

*R' = R–CH(CH$_3$)CH$_2$CH(CH$_3$).

**B.p. 172.5-173.5° (7.5 mm), $n^{25}D$ 1.4421, d_4^{25} 0.878 [11].

TABLE 4. Hydrocarbons, R–CH(CH$_3$)–CH$_2$CH(CH$_3$)CH(CH$_3$)CH$_2$–CH(CH$_3$)–R

R	Yield (in %)	Boiling point at 1 mm	n_D^{20}	d_4^{20}	MR_D		Found (%)		Empirical formula	Calculated (%)		Viscosity at 20° in centistokes	Freezing point
					found	calculated	C	H		C	H		
n -C_6H_{13}	4	141—142°	1.4532	0.8105	103.62	104.31			$C_{22}H_{46}$				
n -C_7H_{15}	12.6	176—177	1.4543	0.8127	112.91	113.60	85.36, 85.10	14.71, 14.81	$C_{24}H_{50}$	85.12	14.88	19.50	—67°
n -C_8H_{17}	18.4	187—188	1.4552	0.8147	122.16	122.90	84.92, 84.87	14.77, 14.76	$C_{26}H_{54}$	85.16	14.84	24.23	—62
n -C_9H_{19}	14.2	203—204	1.4566	0.8172	131.45	132.20	85.19, 85.14	14.66, 14.69	$C_{28}H_{58}$	85.16	14.84	31.54	—58
n -$C_{10}H_{21}$	23.6	211—213	1.4572	0.8188	140.68	141.49	85.20, 85.09	14.80, 15.00	$C_{30}H_{62}$	85.21	14.78	36.57	—51—52
$C_6H_{13}(CH_3)CH$	11.7	153—156	1.4580	0.8235	121.49	122.90	85.32, 85.50	14.57, 14.73	$C_{26}H_{54}$	85.16	14.84	37.39	—54—55
$C_4H_9CH(C_2H_5)CH_2$	12.7	142—143	1.4580	0.8226	121.60	122.90	85.17, 84.91	14.90, 14.69	$C_{26}H_{54}$	85.16	14.84	36.05	—52

4-Methyl-2-undecene. Heptyl bromide (358.5 g; 2 moles) was added in 4 hr to a stirred suspension of 60 g (2.5 moles) of magnesium in 1350 ml of ether. The ether solution was stirred for another hour after all of the bromide had been added, and then the excess magnesium was filtered and the amount of Grignard reagent in the ether solution was determined (by back titration). This was followed by the addition of 251 g (2.4 moles) of 2-chloro-3-pentene in 2.5 hr to the ether solution of heptylmagnesium bromide; after standing overnight the reaction mixture was refluxed for 8 hr, and then it was decomposed with water and 10% hydrochloric acid. The subsequent operations were conventional. After removal of the ether, the residue was vacuum-distilled to yield excess 2-chloro-4-pentene and 231 g (68.5%) of 4-methyl-2-undecene.

4-Methyl-2-bromoundecane. A charge of 215 g (1.28 moles) of the olefin was placed in an Erlenmeyer flask. Then hydrogen bromide was bubbled through the olefin for 29 hr at 0–5°. The increase in weight was 143 g (theory is 104 g). The obtained bromide was washed with water and then with dilute sodium carbonate solution, diluted with an equal volume of ether, and dried over $CaCl_2$. Vacuum-distillation of the reaction mixture resulted in the isolation of unreacted olefin and 241 g (74.3%) of 4-methyl-2-bromoundecane.

2,4-Dimethylundecanoic acid. 4-Methyl-2-bromoundecane (215 g; 0.86 mole) was added in 5 hr to a stirred suspension of 84 g (3.45 moles) of magnesium in 500 ml of ether. The ether solution was stirred for another hour after adding the bromide, and then it was treated with 500 g of solid carbon dioxide over a period of 2.5 hr. After standing for 12 hr the reaction mass was decomposed with water and 10% hydrochloric acid. From the ether layer and the ether extracts of the water layer we isolated 71 g (76.3% yield, based on obtained Grignard reagent) of 2,4-dimethylundecanoic acid and 28.4 g (12.6%) of 8,10,11,13-tetramethyleicosane.

Order of hydrogen bromide addition to β-olefins. Operating as described above in accordance with Scheme (1), we synthesized 2-methyl-4-bromopentane with b.p. 52.5–53° (44 mm), d_4^{20} 1.1576, n_D^{20} 1.4440. This same bromide, prepared in accordance with Scheme (2) from 2-methyl-4-pentanol and hydrogen bromide, had b.p. 51–52° (44 mm), d_4^{20} 1.1585, n_D^{20} 1.4440. Both bromides had the same Raman spectrum.

$\Delta\nu$ cm^{-1}: 149 (2 wide), 230 (1w), 299 (5w), 360 (2), 402 (2), 472 (3w), 544 (10), 620 (7w), 823 (7), 860 (1), 901 (3), 962 (2w), 993 (0), 1052 (1), 1079 (1), 1152 (3w), 1204 (4), 1250 (1), 1343 (2), 1450 (6), 1464 (6), 2870 (10), 2922 (8), 2963 (10), 2989

The second isomer of 2-methyl-4-bromopentane, which could be formed when 2-methyl-3-pentene is reacted with HBr, namely 2-methyl-3-bromopentane, was also obtained by us by reacting hydrogen bromide with 2-methyl-3-pentanol (which was prepared from propionaldehyde and isopropylmagnesium bromide), and had the following constants: b.p. 48–49° (43 mm), d_4^{20} 1.1450, n_D^{20} 1.4438.

Raman spectrum.* $\Delta\nu$ cm^{-1}: 149 (3), 278 (5), 299 (10), 332 (0), 406 (0), 434 (0), 484 (4), 515 (9), 606 (3w), 745 (0w), 787 (2), 809 (4w), 861 (1), 903 (3), 958 (0), 1035 (2), 1065 (1), 1095 (1), 1121 (2), 1147 (4), 1200 (0w), 1228 (1), 1311 (2), 1387 (0w), 1434 (4w), 1448 (4w), 2831 (2), 2874 (10), 2912 (10), 2930 (9), 2965 (10), 2984 (5).

SUMMARY

1. A number of 2-alkyl-3-pentenes were synthesized from 2-chloro-3-pentene and alkylmagnesium bromides.

2. It was shown that only 2-alkyl-4-bromopentanes are formed when hydrogen bromide adds to these β-olefins.

3. A number of C_{12}–C_{16} acids, having either two or three branched chains in the main hydrocarbon chain, were synthesized from 2-alkyl-4-bromopentanes by the Grignard method.

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*The spectra were taken by L A. Leites, to whom the authors express their thanks.

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STUDY OF THE ALKALINE OXIDATION OF ISOPROPYLBENZENE

II. ALKALINE PROTECTION OF THE OXIDATION PROCESS

V. A. Simanov and M. S. Nemtsov

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2153-2160,
July, 1960
Original article submitted June 18, 1959

As had been shown in the previous paper [1], in the alkaline oxidation of isopropylbenzene the process, after a short period of accelerated reaction, proceeds at a slower rate. However, the rate of this process in an alkaline medium is always considerably greater than the oxidation rate of pure isopropylbenzene in the absence of activating additives. Consequently, in the alkaline process an acceleration of the reaction is observed even after the main portion of the free caustic alkali has been consumed. This effect must be explained as being due to the beneficial influence exerted by the salts that are formed in the reaction of the caustic alkali with the acid by-products of the reaction, i.e., with the carbon dioxide and organic acids.

The beneficial influence exerted by these salts may be explained in harmony with the concepts developed earlier for the reaction mechanism of the oxidation of isopropylbenzene involving manganese [2, 4]. These concepts are based on the assumption that the mechanism involves a rupture of the reaction chains due to acidic decomposition of the isopropylbenzene hydroperoxide in accordance with the reaction first described for mineral acids by R. Yu. Udris*, and also by Hock and Lang [3], and later confirmed experimentally for the case of a strong organic acid [4], in accordance with the scheme:

$$C_6H_5C(CH_3)_2OOH \xrightarrow{HCOOH} C_6H_5OH + (CH_3)_2CO.$$

According to the above mentioned concepts [2, 4], the phenol is converted to benzoquinone, which quantitatively binds the free radicals, functioning to propagate the chain oxidation process [5].

As a result, if alkaline salts of weak acids are present in the reaction medium, capable of binding the stronger acids liberated in the oxidation process, and in particular formic acid, then this eliminates the possibility of the acidic decomposition of isopropylbenzene hydroperoxide taking place, and consequently inhibition of the oxidation process is prevented.

To confirm these theories we ran some experiments on the oxidation of quite pure isopropylbenzene, which was obtained by alkylation using aluminum chloride as catalyst (Sample I) in the presence of various alkaline additives, introduced in equivalent amounts. Both the experimental procedure and the method of making the calculations were described earlier [1]. First of all, the kinetic curves plotted in Fig. 1 show that not one of the added alkaline salts gives the initial "jump" of an accelerated rate, characteristic for free caustic alkali. Consequently, not only sodium carbonate, as was mentioned in the previous paper [1], but also the alkaline salts of organic acids are incapable of activating the formation of free radicals, which is the case when the oxidation process is run in the presence of free alkalies. An examination of the curves in Fig. 1 also permits the conclusion

*Cited from [2].

that all of the alkaline additives tend to accelerate the oxidation of isopropylbenzene when compared to running the process without an additive (Curve 1), in which connection this acceleration, hardly noticeable at the very start of reaction, increases with increase in the extent of isopropylbenzene transformation. These observations are found in agreement with the above mentioned concepts regarding the protective action of alkaline additives, which reduces to a binding of the acid by-products formed in the oxidation process. Finally, a comparison of Curves 2–5 in Fig. 1 reveals that the quantitative effect of the acceleration is essentially dependent on the nature of the anion of the alkaline salts, in which connection the accelerating influence, as a first approximation, is inversely proportional to the strength of the acid.

The observations made during the oxidation of comparatively pure isopropylbenzene made it possible to assume that the mentioned additives could also prove effective in the oxidation of a less pure isopropylbenzene and, in particular, in the oxidation of the isopropylbenzene obtained by alkylation using phosphoric acid as the catalyst, which material, as was shown in the previous paper [1], is hardly oxidized at all in the absence of caustic alkali. To verify this we ran some experiments in which sodium stearate was used as the protective additive. In this series of experiments we used two different samples of isopropylbenzene, both obtained by alkylation using phosphoric acid as the catalyst: Sample II, the characteristics of which are given in Table 1 of the previous paper [1], and the same sample, but after it had been treated with 6 successive portions of concd. sulfuric acid for a long time, followed by fractionation through an efficient laboratory column (Sample III). In addition, for comparison in these experiments, the initial formation of free radicals was accomplished either by the thermal decomposition of the large amount of hydroperoxide added to the starting isopropylbenzene, or by the decomposition of azobisisobutyronitrile, the use of which for this purpose was described in the previous paper [1]. The corresponding data are given in Table 1 and they are also plotted as the kinetic curves shown in Figs. 2–4.

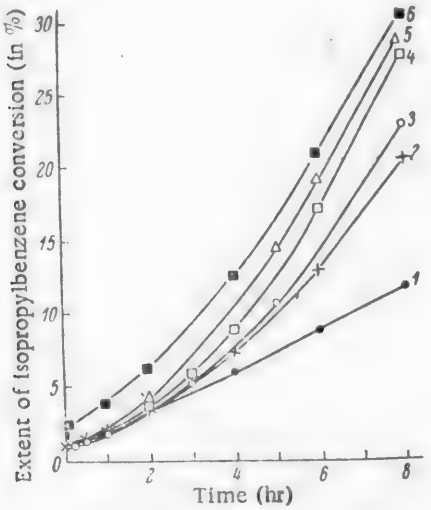

Fig. 1. Kinetics of the oxidation of isopropylbenzene (I) in the presence of equivalent amounts of sodium hydroxide and its salts. 1) Without additive; 2) HCOONa; 3) Na_2CO_3; 4) $C_{17}H_{35}COONa$; 5) C_6H_5COONa; 6) NaOH 0.05%.

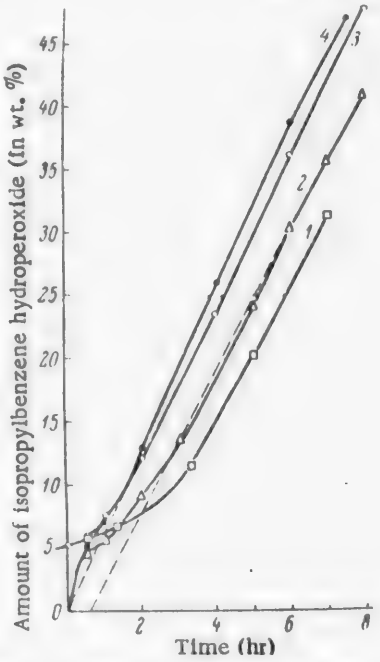

Fig. 2. Kinetics of the oxidation of purified isopropylbenzene (III) in the presence of sodium stearate. 1) Without additive, initiator isopropylbenzene hydroperoxide; 2) likewise, initiator azobisisobutyronitrile; 3) 0.3% $C_{17}H_{35}$·COONa, initiator isopropylbenzene hydroperoxide; 4) likewise, initiator azobisisobutyronitrile.

An examination of the curves in Fig. 2 reveals that in the oxidation of the purified isopropylbenzene the influence of the protective additive on the reaction rate, irrespective of whether the process is initiated by "seeding" with hydroperoxide or by the decomposition of azobisisobutyronitrile, is comparatively small, in which connection the effect of the stearate is primarily reflected in a shortening of the induction period, after which the branches of the curves become almost parallel.

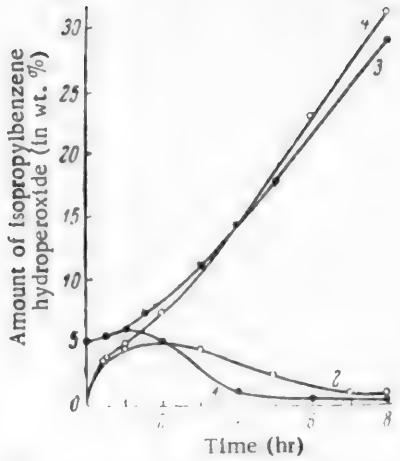

Fig. 3. Kinetics of the oxidation of impure isopropylbenzene (II) in the presence of sodium stearate. 1) Without additive, initiator IPBHP;* 2) likewise, initiator azobisisobutyronitrile; 0.3% $C_{17}H_{35}COONa$, initiator IPBHP; 4) likewise, initiator azobisisobutyronitrile.

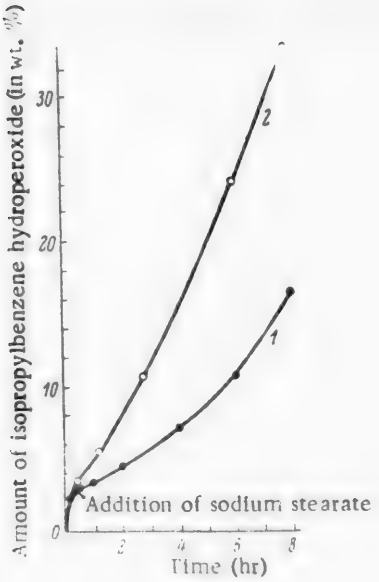

Fig. 4. Effect of the time at which the sodium stearate is added on the kinetics of the oxidation of impure isopropylbenzene (II) (when initiated using azobisisobutyronitrile). 1) $C_{17}H_{35}COONa$ added 30 min after the start of the oxidation process; 2) $C_{17}H_{35}COONa$ added at the start of the process.

An examination of the curves in Fig. 2 reveals that in the oxidation of the purified isopropylbenzene the influence of the protective additive on the reaction rate, irrespective of whether the process is initiated by "seeding" with hydroperoxide or by the decomposition of azobisisobutyronitrile, is comparatively small, in which connection the effect of the stearate is primarily reflected in a shortening of the induction period, after which the branches of the curves become almost parallel.

The fact that some difference exists in the experiments run using different methods of initial initiation also deserves some consideration. Thus, a comparison of Curves 1 and 2 (without sodium stearate) reveals that they diverge after their intersection at the point corresponding to a content of 6% hydroperoxide in the reaction mass, in which connection Curve 2 (using azobisisobutyronitrile as initiator) was practically out of the induction period by this time, whereas Curve 1 for the "hydroperoxide" initiation had failed to reach even the middle of the induction period. An analogous character, although expressed less sharply, is also possessed by Curves 3 and 4 (for the sodium stearate protected process). Besides this, some difference in the reaction rates is also observed for the process outside the limits of the induction period. Thus, the slope of the curves in the region where the extent of oxidation exceeds 20% is 12–13% greater for the processes initiated using azobisisobutyronitrile than when the oxidation is initiated through the decomposition of the hydroperoxide itself. It is possible to explain this by assuming that the isopropylbenzene hydroperoxide used as the "seed" contained some harmful impurities, which were formed in the preparation of the material and during storage. Harmful impurities were not introduced into the starting reaction mass in the case of where azobisisobutyronitrile was used.

An important result deriving from the above discussed experiments is the observation that harmful impurities, present even in the isopropylbenzene that had been purified with extreme care in advance, exert an inhibiting action on the process. Thus, in the experiments initiated with azobisisobutyronitrile (Curves 2 and 4), i.e., where the possibility of introducing harmful impurities with the hydroperoxide is excluded, a substantial reduction in the length of the induction period was observed when sodium stearate was added. This result could appear only as the consequence of eliminating the harmful action of the impurities present in the starting isopropylbenzene, and not of the substances formed during the oxidation of the isopropylbenzene itself. In support of this conclusion

*Isopropylbenzene hydroperoxide.

TABLE 1

Effect of the Protective Addition of Sodium Stearate on the Oxidation of Pure and Impure Isopropylbenzene, Obtained by Alkylation Using Phosphoric Acid as the Catalyst

Starting isopropylbenzene		Pure (Sample III)								Impure (Sample II)							
method of initiation		IPBHP* (5%)				Azobisisobutyronitrile (0.1%)				IPBHP (5%)				Azobisisobutyronitrile (0.1%)			
expt. no.		1		2		3		4		5		6		7		8	
addition of sodium stearate (in wt. %)		none		0.3		none		0.3		none		0.3		none		0.3	
indices of the process		amount of IPBHP (in wt. %)	decomposition of IPBHP (in %)	amount of IPBHP (in wt. %)	decomposition of IPBHP (in %)	amount of IPBHP (in wt. %)	decomposition of IPBHP (in %)	amount of IPBHP (in wt. %)	decomposition of IPBHP (in %)	amount of IPBHP (in wt. %)	decomposition of IPBHP (in %)	amount of IPBHP (in wt. %)	decomposition of IPBHP (in %)	amount of IPBHP (in wt. %)	decomposition of IPBHP (in %)	amount of IPBHP (in wt. %)	decomposition of IPBHP (in %)
Time (in hr)	0	5.0	—	5.0	—	0	—	0	—	5.0	—	5.0	—	0	—	0	—
	0.5	5.7	0	5.8	0	4.5	0	4.9	0	—	—	5.4	0	3.7	0	3.5	0
	1.0	—	—	7.6	0	5.5	2	7.1	0	6.1	3	—	—	4.5	0	4.8	0
	1.3	6.7	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1.5	—	—	—	—	—	—	—	—	—	—	7.2	0	—	—	—	—
	2.0	—	—	12.1	1	9.1	0	12.9	0	4.1	53	—	—	—	—	7.3	0
	3.0	—	—	—	—	13.6	0	—	—	—	—	11.1	0	4.4	38	—	—
	3.3	11.5	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	4.0	—	—	23.6	0	—	—	26.2	5	1.9	92	—	—	—	—	14.3	0
	5.0	20.3	2	—	—	24.2	2	—	—	—	—	17.9	1	2.4	74	—	—
	6.0	—	—	36.3	8.5	30.6	3	38.8	8	0.5	96	—	—	—	—	23.1	4
	7.0	31.5	3	—	—	35.8	8	—	—	—	—	—	—	0.9	94	—	—
	7.5	—	—	—	—	—	—	47.1	13	—	—	—	—	—	—	—	—
	8.0	—	—	48.0	11	41.2	7	—	—	0.3	98	29.2	7	0.8	95	32.6	7

* Isopropylbenzene hydroperoxide.

TABLE 2

Oxidation of Impure Isopropylbenzene (II) in the Presence of Equivalent Amounts of NaOH and $C_{17}H_{35}COONa$

Additive	Time of oxidation (in minutes)																			
	0		10		20		30		60		120		240		360		480			
	% HP	% decomp.	% HP	% decomp.	% HP	% decomp.	% HP	% decomp.	% HP	% decomp.	% HP	% decomp.	% HP	% decomp.	% HP	% decomp.	% HP	% decomp.		
Without additive	Not oxidized																			
NaOH, 0.05 wt. %	0.40	—	0.56	21	1.15	15	1.40	14	1.90	15	3.40	13	8.4	5	16.1	5	26.4	6		
$C_{17}H_{35}COONa$, equiv. to 0.05 wt. % NaOH	0.40	—	0.42	0	0.46	0	0.48	0	0.61	0	1.20	0	3.2	0	9.2	2	18.1	4		

we have drawn tangents to the linear segments of Curves 2 and 4 (see the dotted lines in Fig. 2), from which it can be seen that the tangent for the experiment using sodium stearate passes through the origin, while for the unprotected process the tangent intersects the abscissa at a point roughly corresponding to the time consumed in overcoming the inhibiting effect of the harmful impurities present in the starting isopropylbenzene.

In accordance with these considerations it could be expected that sodium stearate would exert a much greater protective action in the oxidation of the impure isopropylbenzene (Sample II), and this was confirmed by the experimental data, which are plotted in Fig. 3. Here Curves 1 and 2 for the experiments without sodium stearate show that without alkaline protection the oxidation of the impure isopropylbenzene, with both methods of initiation, hardly goes at all and is accompanied by a nearly complete decomposition of the hydroperoxide (see Expts. 5 and 7 in Table 1). When 0.3 wt. % of sodium stearate is added, the oxidation process, irrespective of whether it is initiated using hydroperoxide or azobisisobutyronitrile, goes at a sufficiently rapid rate and with little decomposition of the isopropylbenzene hydroperoxide (see Curves 3 and 4 in Fig. 3 and Expts. 6 and 8 in Table 1).

As a result, the use of sodium stearate as a protective agent in the oxidation of isopropylbenzene proved to be effective not only as regards the inhibiting action exerted by the substances formed during the oxidation of the purified isopropylbenzene, but also as regards the inhibiting action exerted by the large amounts of harmful impurities present in the starting impure isopropylbenzene. As was shown in Table 2, the difference between the process for the oxidation of the impure isopropylbenzene using sodium stearate and running the alkaline process in the presence of an equivalent amount of sodium hydroxide consists in some reduction in the efficiency of the process due to a lengthening of the induction period, but with a noticeable decrease in the degree of hydroperoxide decomposition at small values for the extent of isopropylbenzene conversion.

Consequently, in the oxidation of isopropylbenzene, whenit is desired to obtain the purest isopropylbenzene hydroperoxide possible, which is especially important in the production of phenol and acetone, the use of sodium stearate or other alkaline salts of weak acids as protective additives can possess considerable practical interest.

A comparison of Curves 3 and 4 in Fig. 3 also makes it possible to corroborate the advantages mentioned above as regards the use of azobisisobutyronitrile to initiate the oxidation process when compared with isopropylbenzene hydroperoxide "seeding". Thus, Curve 4 for the azobisisobutyronitrile has a greater slope toward the ordinate than does Curve 3 (for the hydroperoxide), which, with all of the other conditions constant, corresponds to an acceleration of the process by approximately 15-20%. This observation can also possess practical interest, since azobisisobutyronitrile is a readily available technical product, sold under the trade name of "Porofor N".

The shape of Curves 1 and 2 in Fig. 3 (for the experiments not protected by sodium stearate) makes it possible to arrive at

some conclusions regarding the character of the processes inhibiting the oxidation under the influence of the harmful impurities present in the isopropylbenzene. Thus, at the start of these experiments a distinct increase is observed in the concentration of isopropylbenzene hydroperoxide in the reaction mass, with a relatively small consumption of it (see Table 1), and only after a certain maximum has been reached does the concentration of the hydroperoxide decrease, with a simultaneous sharp increase in the extent of its decomposition. These facts make it possible to assume that the impurities initially present in the starting crude are incapable by themselves of inhibiting the oxidation process, and that only the acidic products of their transformation during the oxidation process manifest an inhibiting action. Inasmuch as the harmful influence of these products is removed by alkaline additives (see Curves 3 and 4 in Fig. 3), it may be assumed that they have an acid character, the same as the organic acids that are formed as by-products in the oxidation of isopropylbenzene itself. A comparison of Curves 1 and 2 also lends support to the above mentioned postulation that the process initiated by azobisisobutyronitrile proceeds better than does the "hydroperoxide" process, due to the introduction with the hydroperoxide of impurities that are harmful for the process. In accordance with this, Curve 1 drops more rapidly with time and is characterized by higher rates of hydroperoxide decomposition (see Expt. 5 in Table 1).

The data presented above indicate that when the impure isopropylbenzene (Sample II) is oxidized in the presence of protective alkaline additives, the same as when the process is run with free alkali present, a decomposition of the harmful impurities occurs in the initial period of reaction, i.e., the isopropylbenzene undergoes its own kind of purification, after which the process proceeds normally at a more rapid rate.

A similar oxidative purification is also accomplished in the absence of alkaline additives if a sufficiently pure isopropylbenzene (Sample III) is used (see Curve 1 in Fig. 2 and Expt. 1 in Table 1). However, the efficiency of such a purification proves to be inadequate for an isopropylbenzene (Sample II) containing large amounts of harmful impurities, as was observed for the impure isopropylbenzene obtained by alkylation in the presence of phosphoric acid (see Curves 1 and 2 in Fig. 3), and in this case only the introduction of an alkaline additive could prevent a complete stoppage of the process.

The protective action of alkaline additives, and in particular of sodium stearate, is manifested not only in the period of the stationary oxidation of the isopropylbenzene itself, where the acid by-products of the transformation of the latter are bound, but also in the initial stage of the process, corresponding to the period of the oxidative purification of the starting isopropylbenzene. To determine the specific effect of protective alkaline additives in each of these periods we ran a number of experiments (using azobisisobutyronitrile as the initiator), the results of which are shown in Fig. 4. Curve 1, corresponding to the experiment where the sodium stearate was added 30 min after the start of oxidation, indicates a substantial reduction in the reaction rate when compared with the experiment where the sodium stearate was added to the starting isopropylbenzene (Curve 2), in which connection the initial rise in the amount of hydroperoxide during the period of azobisisobutyronitrile decomposition proved to be greater in the latter experiment than in the case where the sodium stearate was added after 30 min.

These data permit the conclusion that the protective role of alkaline additives is especially great at the start of the process, i.e., during the period of decomposing the harmful impurities, since the acid products formed in the oxidation of the latter, not being bound in time, lead to a large accumulation in the reaction mass of substances inhibiting the process, which no longer can be rendered harmless by the later addition of alkaline salts.

As a result, the mechanism for the inhibiting action of the harmful impurities present in technical isopropylbenzene can be regarded as identical with the mechanism for the inhibition of the process by the side products of the oxidation of isopropylbenzene itself, reducing to a development of the reaction for the decomposition of isopropylbenzene hydroperoxide to phenol under the influence of strong acids.

SUMMARY

1. The concepts regarding the inhibition of the oxidation of isopropylbenzene by the products of the acid decomposition of its hydroperoxide were confirmed. The addition of the alkaline salts of weak organic acids inhibits the reaction for the acid decomposition of isopropylbenzene hydroperoxide by binding the strong organic acids formed in the oxidation process.

2. Salts of organic acids do not activate the alkaline decomposition of isopropylbenzene hydroperoxide with the formation of free radicals, as was observed in the presence of free caustic alkali.

3. Alkaline salts of organic acids accelerate the oxidation of isopropylbenzene when compared to running the process without alkaline additives. The quantitative effect of the acceleration depends on the nature of the anion of the acid and as a first approximation is inversely proportional to the strength of the acid.

4. The harmful impurities present in technical isopropylbenzene do not by themselves inhibit the oxidation of isopropylbenzene, but instead it is the acid products of their transformation that function as the inhibitors.

5. The greatest effect of the protective additives is observed in the initial stage of the oxidation process, where an intense accumulation of inhibiting substances occurs.

6. The inhibiting effect exerted by the harmful impurities present in technical isopropylbenzene is identical in its character to inhibition of the oxidation process by the side products of the acid decomposition of isopropylbenzene hydroperoxide.

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*Original Russian pagination. See C. B. translation.

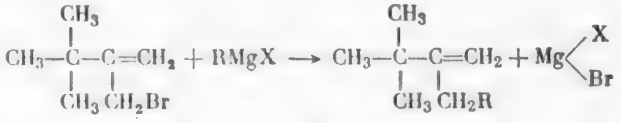
PREPARATION OF ALLYLIC TYPE BROMIDE $C_7H_{13}Br$ AND ITS CONDENSATION BY THE GRIGNARD – WURTZ REACTION

E. B. Sokolova, M. P Shebanova, and A. P. Mrnkova

D. I. Mendeleev Moscow Chemical-Technological Institute

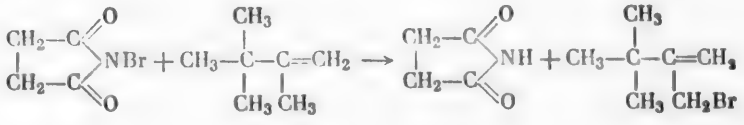
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2161-2164,
July, 1960
Original article submitted June 26, 1959

It is known that the use of allylic type halides in the Grignard–Wurtz reaction leads to a substantial increase in the yield of condensation product. However, here the halides as a rule undergo allylic rearrangement, resulting in the formation of a mixture of isomeric compounds, the separation of which requires the use of highly efficient rectification equipment. In this paper we were the first to synthesize the allylic type halide 3-(bromomethyl)-2,2-dimethyl-3-butene, the structure of which excludes the possibility of obtaining isomeric compounds when it is used in the Grignard–Wurtz reaction.



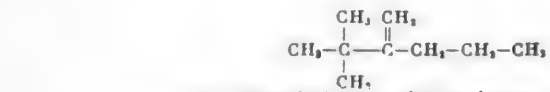
A number of new hydrocarbons of composition C_9–C_{14} were obtained by this scheme in quite good yields (30–70%). The indicated halide was condensed with ethyl-, n-butyl-, n-heptyl- and benzylmagnesium bromides and with tert-butylmagnesium chloride. In addition, the 3-(bromomethyl)-2,2-dimethyl-3-butene was condensed by the Wurtz reaction.

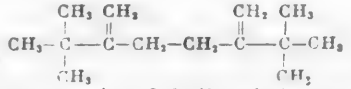
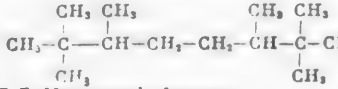
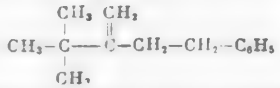
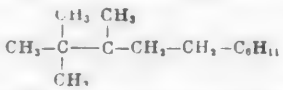
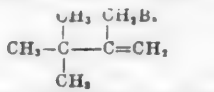
The starting 3-(bromomethyl)-2,2-dimethyl-3-butene was obtained in 40.5% yield by the bromination of 2,2,3-trimethyl-3-butene with N-bromosuccinimide (prepared by the procedure given in [1]) in accordance with the scheme:



The conditions for brominating the 2,2,3-trimethyl-3-butene were taken from [2], where examples of brominating monoolefins with N-bromosuccinimide for the purpose of putting the halogen in the allyl position are given.

Condensation of the obtained allylic type bromide with alkyl (aryl) magnesium halides was carried out in the conventional Grignard apparatus using a modification of the method described in [3]. Specifically, this modification consisted in adding double the theoretical amount of organomagnesium compound to the allylic type halide. In all cases the condensation was run at the boiling point of diethyl ether. After the usual treatment, the reaction products were vacuum-distilled twice from sodium, employing either a precise fractionation column or a long Vigreux column.

Formula and name of hydrocarbon	Yield (in %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Found (%)		Empirical formula	Calculated (%)	
					found	calculated	C	H		C	H
 2,2,-Dimethyl-3-methylenehexane	64.0	127—127.5° (760)	1.4150	0.7315	43.21	43.30	85.75, 85.76	14.45, 14.37	C_9H_{18}	85.63	14.37
2,2,-Dimethyl-3-methyleneoctane	34.0 *	70 (36)	1.4396	0.7736	52.50	52.53	85.72, 85.56	14.35, 14.40	$C_{11}H_{22}$	85.63	14.37
2,2,5,5,-Tetramethyl-3-methylenehexane	70.5	62—63 (15)	1.4520	0.7939	52.42	52.53	85.73, 85.69	14.38, 14.46	$C_{11}H_{22}$	85.63	14.37
2,2-Dimethyl-3-methyleneundecane	50.0	90 (8)	1.4440	0.7887	66.13	66.39	85.72, 85.66	14.39, 14.42	$C_{14}H_{28}$	85.63	14.37
2,2,3-Trimethylundecane		86 (8)	1.4340	0.7714	66.95	66.85	84.81, 84.72	15.21, 15.32	$C_{14}H_{30}$	84.76	15.24

Formula and name of hydrocarbon	Yield (in %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Found (%) C	Found (%) H	Empirical formula	Calculated (%) C	Calculated (%) H
 2,2,7,7-Tetramethyl-3,6-dimethyleneoctane	26.7	88 (13)	1.4550	0.8016	65.78	65.92	86.79, 86.57	13.50, 13.51	$C_{14}H_{26}$	86.52	13.48
 2,2,3,6,7,7-Hexamethyloctane		72 (5)	1.4380	0.7806	66.72	66.85	84.73, 84.75	15.26, 15.28	$C_{14}H_{30}$	84.76	15.24
 2,2-Dimethyl-3-methylene-5-phenylpentane	53.0	88 (6)	1.5030	0.8824	63.08	62.78	89.33, 89.34	10.61, 10.68	$C_{14}H_{20}$	89.30	10.70
 2,2,3-Trimethyl-5-cyclohexylpentane		105 (15)	1.4550	0.8255	64.53	64.65	85.57, 85.68	14.30, 14.32	$C_{14}H_{28}$	85.63	14.37
 3-(Bromomethyl)-2,2-dimethyl-3-butene**	40.5	51 (7)	1.4755	1.1988	41.63	41.82					

* In this experiment the allylic type bromide was added to the organomagnesium compound.

** Found %: Br 44.41. $C_7H_{13}Br$. Calculated %: Br 45.13.

The condensation of 3-(bromomethyl)-2,2-dimethyl-3-butene by the Wurtz reaction (using metallic sodium) was carried out employing the procedure described in [4].

One of the condensation products, 2,2-dimethyl-3-methylenehexane, was oxidized with 10% potassium permanganate solution. The obtained oxidation products, propyl tert-butyl ketone and formic acid, confirm the structure of the above named hydrocarbon. In the case of 2,2,3,6,7,7-hexamethyloctane we took the infrared spectrum of the compound, and here the spectral data confirmed the presence of eight methyl and two methylene groups in the hydrocarbon molecule. 2,2,7,7-Tetramethyl-3,6-dimethyleneoctane, 2,2-dimethyl-3-methyleneundecane and 2,2-dimethyl-3-methylene-5-phenylpentane were converted to the corresponding saturated hydrocarbons (isoparaffins and alkyl-substituted cyclohexane) by hydrogenation in an autoclave over nickel catalyst at 160–170° and an initial H_2 pressure of 100 atm. The properties of the compounds, obtained for the first time, are given in the Table.

SUMMARY

1. The bromination of 2,2,3-trimethyl-3-butene with N-bromosuccinimide gave the new allylic type halide, 3-(bromomethyl)-2,3-dimethyl-3-butene, the structure of which excludes the possibility of allylic rearrangement when the compound is condensed with alkyl (aryl) magnesium halides.

2. The condensation of 3-(bromomethyl)-2,2-dimethyl-3-butene with alkylmagnesium halides, and also by the Wurtz reaction, gave in high yield (30–70%) nine new hydrocarbons of composition C_9–C_{14}, having a branched structure.

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*Original Russian pagination. See C. B. translation.

IDENTIFICATION OF ALKYLBENZENES

II. ANALYSIS OF BINARY MIXTURES OF ACYLAMINO DERIVATIVES OF 2-PHENYLBUTANE AND 3-PHENYLPENTANE

T. E. Zalesskaya and L. E. Zhuravleva

Leningrad Technological Institute of the Cellulose-Paper Industry
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2164-2166,
July, 1960
Original article submitted June 23, 1959

When making a detailed study of the isomeric transformations of carbonyl compounds the need arises at times of identifying the aromatic hydrocarbons, adjacent members of a homologous series, found in admixture with each other.

In order to identify 2-phenylbutane and 3-phenylpentane, found in admixture with each other, we synthesized these hydrocarbons, prepared their acylamino derivatives, and then subjected binary mixtures of the corresponding derivatives to thermal analysis under such conditions as would permit operating with small amounts of the test materials.

The melting points of mixtures of the benzoyl derivatives of 2-(p-aminophenyl) butane and 3-(p-aminophenyl) pentane were read, as were also those of the acetyl and benzoyl derivatives of 2-(2,4-diaminophenyl) butane and 3-(2,4-diaminophenyl) pentane.

EXPERIMENTAL

The synthesis of 2-phenylbutane and its acylamino derivatives was described earlier [1]. The 3-phenylpentane derivatives were obtained in a similar manner.

3-Phenylpentane. To prepare this compound we took 31 g of diethylphenylcarbinol, synthesized by the Grignard reaction, and having b.p. 116.5–118° at 24 mm (from [2]: b.p. 110–112° at 20 mm), and reduced it with hydrogen iodide (7 g of red phosphorus, 25 ml of hydriodic acid with b.p. 127°, and 34 g of iodine). The yield of the hydrocarbon was 24 g.

B.p. 78–79° at 18 mm, 79–80° at 19 mm, d^{15}_4 0.8667, d^0_4 0.8780.

From [3], 3-phenylpentane has b.p. 73–74° at 12 mm.

3-(p-Nitrophenyl) pentane and 3-(2,4-dinitrophenyl) pentane. 3-Phenylpentane was nitrated under the conditions used to nitrate 2-phenylbutane [1]. The following fractions were obtained when 17.5 g of the product was distilled at 14 mm: 1st, b.p. 160–182°, 11.1 g; 2nd, b.p. 187–188°, 9.7 g; residue (tar), about 1 g. The 1st fraction was redistilled twice. We obtained 7 g of 3-(p-nitrophenyl) pentane as a pale yellow liquid with a characteristic odor.

B.p. 148–149° at 13 mm, d^{20}_4 1.04881, d^0_4 1.06328, n^{20}_D 1.52521, MR_D 56.41; Calc. 55.60.

Found %: N 7.53. $C_{11}H_{15}O_2N$. Calculated %: N 7.25.

Oxidation of the substance with 1.5% potassium permanganate solution gave p-nitrobenzoic acid (m.p. 238°).

The 2nd fraction quickly crystallized to a pale yellow mass. Recrystallization from alcohol gave 3-(2,4-dinitrophenyl) pentane with m.p. 54–55°.

Found %: N 11.80, 11.87. $C_{11}H_{14}O_4N_2$. Calculated %: N 11.76.

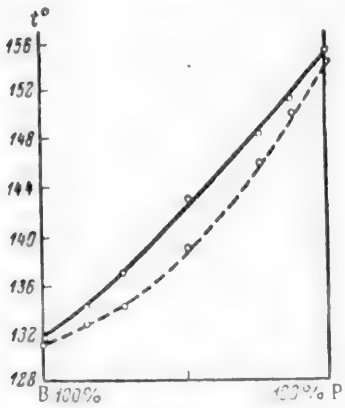

Fig. 1. Melting points of binary mixtures of p-benzoylamino derivatives of 2-phenylbutane and 3-phenylpentane.

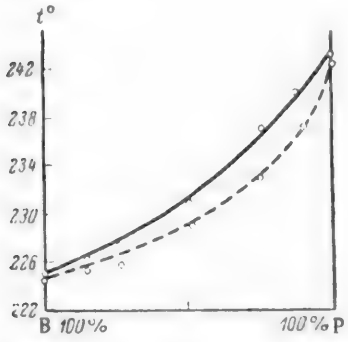

Fig. 3. Melting points of binary mixtures of 2,4-dibenzoylamino derivatives of 2-phenylbutane and 3-phenylpentane.

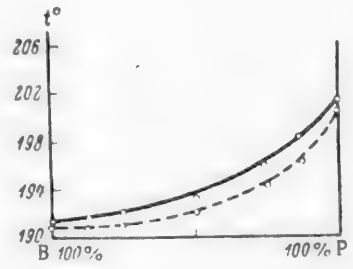

Fig. 2. Melting points of binary mixtures of 2,4-diacetylamino derivatives of 2-phenylbutane and 3-phenylpentane.

The reduction of 3-(p-nitrophenyl) pentane was carried out with tin and hydrochloric acid, employing the same conditions as were used to reduce the corresponding nitro derivative of 2-phenylbutane. From 8.2 g of the p-nitro compound we obtained 4 g of 3-(p-aminophenyl) pentane; a colorless liquid that turned red on storage.

B.p. 126° at 14 mm, d^{20}_4 0.9369, d^0_4 0.9510, $n^{20}D$ 1.52225, MR_D 53.08; Calc. 52.82. Found %: N 8.71. $C_{11}H_{17}N$. Calculated %: N 8.58.

The reduction of 3-(2,4-dinitrophenyl) pentane was also carried out with tin and hydrochloric acid. From 4.25 g of the dinitro compound we obtained 2.9 g of the crude diamine, which was converted to the acyl derivative without prior purification.

3-(p-Benzoylaminophenyl) pentane was obtained in a yield of 1.7 g from 1.8 g of the amine by the Schotten-Baumann method. Recrystallization of the compound from 80% alcohol gave needle crystals that formed layers of glistening plates; m.p. 154.4-155°. From the data in literature, m.p. 154° [4].

Found %: N 5.29, 5.44. $C_{18}H_{21}ON$. Calculated %: N 5.24.

3-(2,4-Diacetylaminophenyl) pentane was obtained in a yield of 1.8 g from 1.4 g of the diamine. After recrystallization from alcohol, m.p. 200.6–201.4°. From the literature, m.p. 199–200° [4].

3-(2,4-Dibenzoylaminophenyl) pentane were prepared by the Schotten-Baumann method. Recrystallization from butyl alcohol gave the compound as fine, slightly yellow crystals with m.p. 243–243.4°.

Found %: N 7.49. $C_{25}H_{26}O_2N_2$ Calculated %: N 7.25.

Thermal analysis. Mixtures were prepared from the corresponding pairs of synthesized acylamino derivatives of 2-phenylbutane and 3-phenylpentane and their melting points were read. The analysis method used was that described for investigating the isomeric $C_{10}H_{14}$ hydrocarbon pairs [1]. The obtained readings are plotted as curves in the coordinates: percent composition–melting point (Figs. 1–3). The left side of each diagram corresponds to 100% 2-phenylbutane derivative (B), and the right side corresponds to 100% 3-phenylpentane derivative (P).

Under the conditions of the investigation, not only the temperature at which the solid phase is observed to disappear, but also the temperature at which the liquid phase appears, is of interest for characterizing each of the mixtures. For this reason we have plotted in the diagrams the fusion curves that were obtained on the basis of reading the points of the start and end of melting of the mixtures.

SUMMARY

In order to identify 2-phenylbutane and 3-phenylpentane, found in admixture with each other, we investigated the melting points of binary mixtures of the p-benzoylamino, 2,4-dibenzoylamino and 2,4-diacetylamino derivatives of the indicated hydrocarbons. The experimental readings obtained are plotted in the diagrams.

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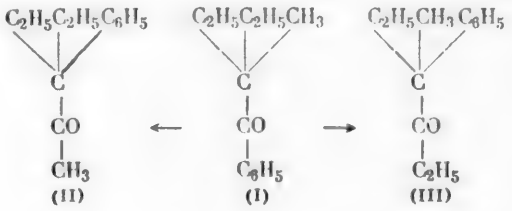
CONCERNING THE CATALYTIC TRANSFORMATIONS OF KETONES. ISOMERIZATION OF α, α-METHYLETHYLBUTYROPHENONE

T. E. Zalesskaya

Leningrad Technological Institute of the Cellulose-Paper Industry
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2166-2170, July, 1960
Original article submitted June 23, 1959

Several cases of the isomeric transformations of α-alkyl-substituted acetophenones are known [1–3]. A shift of the methyl group was observed in the case where both methyl and ethyl were present in the ketone.

To obtain conclusive data on the migration of methyl and ethyl under analogous conditions (when treated with strong mineral acid) it seemed of interest to make a study of the isomeric transformation of α, α-methylethylbutyrophenone (I) when it is heated with zinc chloride. The results of this study revealed that the isomerization goes in two directions, with the formation of 3-ethyl-3-phenyl-2-pentanone (II) and 4-methyl-4-phenyl-3-hexanone (III), in which connection the first direction is by far the more predominant.



On the basis of this information it is possible to conclude that when ketones containing both methyl and ethyl groups are isomerized it is the methyl group that shows predominant shift. And if the formation of a pair of isomeric ketones was not detected earlier, then this is apparently explained by an insufficiently close attention on the part of the experimenter and the difficulty of detecting small amounts of the second isomeric ketones when their formation is statistically less probable than in the case of the ketone investigated in the present paper.

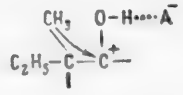
Here it is interesting to mention that in the molecular rearrangement of pinacols, containing both methyl and ethyl, it is the ethyl, and not the methyl, that shows predominant shift [4, 5].

In the light of the concepts developed by the author of the present paper regarding the mechanism of the dehydration of α-glycols and the isomerization of carbonyl compounds [6], such alternative behavior of hydrocarbon groups during shift is explained by the opposite direction of the polarization of the bonds of these groups, differing in the magnitude of polarizability, during reaction.

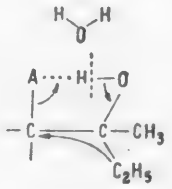
Further discussion is based on the concept that the polarizability of a hydrocarbon group depends on the structure and length of its chain, but is independent of the direction, direct or reverse, in which the polarizing action acts on the hydrocarbon group, under the condition that is is always the same end of the chain that is subjected to this action

We will limit ourselves to ketones and pinacols containing methyl and ethyl groups. The polarizability of $C_2H_5 > CH_3$. When the ketone combines with acid HA the electrophilic center attracts the groups. The greater

polarizability of the C_2H_5 group strengthens its bond with the α-carbon, and consequently it is the less polarized CH_3 group that shifts.



The dehydration product obtained from the combining of α-glycol with acid HA is subjected to hydrolysis, which results in formation of the carbonyl group and migration of the hydrocarbon group. Here the more highly



polarized C_2H_5 group shifts, since its bond with the carbonyl carbon is weakened to a greater degree than in the case of the methyl group when it is displaced by the electrons of the formed carbonyl group.

The observed predominant, but not exclusive shift of the ethyl group (in the case of pinacols) and of the methyl (in the case of ketones) can be explained by the comparatively small difference in the values of the polarizability of the methyl and ethyl groups. Consequently, together with the polar factor, the statistical factor of the probable formation of a second isomeric reaction product also enters into the picture here.

EXPERIMENTAL

α, α-Methylethylbutyrophenone was prepared by heating sec-butyl phenyl ketone (32 g) [7] with sodium amide (10 g) and ethyl iodide (50 g) in 150 ml benzene solution. After isolation and drying (Na_2SO_4), the reaction product was distilled. The following fractions were isolated at a pressure of 12 mm:

1st, b.p. 116-122°, 1.7 g; 2nd, b.p. 122-128°, 26 g; 3rd, b.p. 129–146°, 3 g; residue, 3 g.

After two distillations of the 2nd fraction we obtained 22 g of the ketone with b.p. 125–126° (12 mm); from [8]: b.p. 125–126°; from [9]: b.p. 120–121° (9 mm).

Oxime, m.p. 120.8–121° (from alcohol); from [8]: m.p. 121°; from [9]: m.p. 120.5°.

We were unable to obtain the semicarbazone. Other investigators, who had synthesized the given ketone, were also unable to obtain the semicarbazone.

Isomerization of α, α-methylethylbutyrophenone. Twenty grams of the ketone was added in 4 hr from a dropping funnel to 35 g of $ZnCl_2$ at a bath temperature of 320–325°. The reaction products were steam-distilled, extracted with ether, and dried over sodium sulfate; distillation at 7 mm gave the following fractions:

1st, b.p. 106-114°, 3 drops; 2nd, b.p. 114–116°, 5.1 g; 3rd, b.p. 116–117°, 4.3 g; 4th, b.p. 117–120°, 2 g; residue, 0.8 g.

The 2nd and 3rd fractions were distilled separately at 7 mm. We obtained: 1st fraction, b.p. 113–114°, 1.7 g; 2nd fraction, b.p. 115–117°, 5.0 g; 3rd fraction, b.p. 117–120°, 1.8 g.

Analysis of substance with b.p. 113–114° (7 mm).

Found %: C 82.24; H 9.67. $C_{13}H_{18}O$. Calculated %: C 82.06; H 9.52.

Analysis of substance with b.p. 115–117° (7 mm).

Found %: C 81.91, 82.27; H 9.39, 9.41. $C_{13}H_{18}O$. Calculated %: C 82.06; H 9.52.

The range in the boiling point of the substance, together with the numerical analysis data, corresponding to the empirical formula of the ketone, served as evidence that isomerization had taken place. Attempts to prepare crystalline derivatives of the $C_{13}H_{18}O$ ketones proved unsuccessful. Consequently, to confirm the fact that isomerization had taken place and also to elucidate the structure of the ketones, the obtained ketonic fraction was subjected to alkaline cleavage.

1. Action of alcoholic potassium hydroxide solution. Mixtures composed of 4.5 g of the substance (mixed ketones with b.p. 113–117° at 7 mm), 10 g of KOH and 30 ml of alcohol were heated in sealed glass tubes at 130–140° for 4 hr. After adding water, the reaction mixture was saturated with carbon dioxide gas. The neutral reaction products were extracted with ether. The ether extract was dried over $CaCl_2$. Distillation at 20 mm gave the following fractions:

1st, b.p. 69–79°, 0.2 g; 2nd, b.p. 79–92°, 1.8 g; residue, 0.7 g.

Analysis of the substance with b.p. 79–92° at 20 mm.

Found %: C 89.22; H 10.58. $C_{10}H_{14}$. Calculated %: C 89.48; H 10.52. $C_{11}H_{16}$. Calculated %: C 89.10; H 10.90.

The isolated mixture of hydrocarbons may be considered to be a mixture of 2-phenylbutane and 2-phenylpentane. For purposes of proof and making a quantitative estimate of the proportions of the components, the mixture of hydrocarbons was converted to a mixture of the dibenzoylamino derivatives.

2) Nitration of mixture of hydrocarbons with b.p. 69–92° (20 mm) and reduction of the nitro compounds. The nitrating mixture used to obtain the dinitro compounds was composed of one volume of HNO_3 (d 1.5) and two volumes of H_2SO_4 (d 1.84). With rapid stirring and cooling, 8 ml of the nitrating mixture was added to 1.5 g of the substance at such a rate that the temperature inside the vessel did not rise above 5°. At the end of reaction the mixture was poured over ice and extracted with ether. The ether layer after washing with water was distilled to remove the ether, and the residue was treated with 8 g of granulated tin, 8 ml of hydrochloric acid and 3 ml of alcohol. At the end of reduction the hot liquid was decanted from the unreacted tin; the latter was washed with water, which was then added to the remainder of the solution.

3) Preparation and investigation of benzoylamino derivatives. The mixed amines were isolated from a solution of the salts by the addition of sodium hydroxide and then were extracted with ether. A part of the ether was removed, and 1.5 ml of benzoyl chloride and 5 ml of 2N NaOH solution were added to the residue with cooling and stirring. The isolated mixture of benzoylamino derivatives was recrystallized. Treatment with 80% alcohol (in which the monobenzoylamino derivatives prove to be more soluble) enabled us to isolate 0.03 g of crystals from the alcohol solution, which after purification by boiling with animal charcoal and recrystallization from alcohol had m.p. 139–144.2°, which is approximately the same as the melting point of a 1:1 mixture of the p-benzoylamino derivatives of 2-phenylbutane and 3-phenylpentane, which was prepared and investigated in a separate series of experiments [10]. Recrystallization of the alcohol insoluble portion of the substance from butyl alcohol gave 0.62 g of fine, nearly colorless crystals with m.p. 228.7–236.7°. When this melting point was compared with the melting points of mixtures of the dibenzoylamino derivatives [10] it was possible to conclude that an impurity was present in the mixture of diamine derivatives. The crystals were subjected to fractional crystallization from butanol and from ethanol. Here we isolated 0.152 g of substance with m.p. 243–243.5° and 0.082 g of substance with m.p. 225.1–226.2°. From the melting point the first substance is 3-(2,4-dibenzoylaminophenyl)-pentane, which was confirmed by the fact that the melting point was not depressed when the substance was mixed with the authentic product.

Analysis of the substance with m.p. 243–243.5°.

Found %: N 7.49. $C_{25}H_{26}O_2N_2$. Calculated %: N 7.25.

The crystals with m.p. 225.1–226.2° are a mixture of the 2,4-dibenzoylamino derivatives of 2-phenylbutane (90%) and 3-phenylpentane (10%). This conclusion was confirmed by the mixed melting point with a 9:1 mixture of the authentic derivatives of 2-phenylbutane and 3-phenylpentane, which was not depressed.

In summary, an investigation of the benzoylamino derivatives revealed that the mixture of hydrocarbons (b.p. 69–92° at 20 mm) obtained in the alkaline cleavage of the ketones is a mixture of 2-phenylbutane and 3-phenylpentane, with a predominance of the latter.

SUMMARY

1. A study was made of the isomeric transformation of α, α-methylethylbutyrophenone when it is heated with zinc chloride, in which connection it was observed for the first time that the isomerization of the ketone goes in two directions, with the formation of 3-ethyl-3-phenyl-2-pentanone and 4-methyl-4-phenyl-3-hexanone.

2. In the isomerization of α, α-methylethyl-substituted acetophenones it is the methyl group that migrates in preference to the ethyl.

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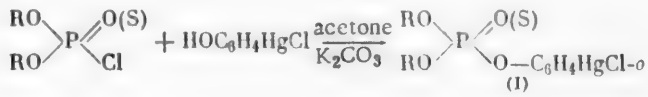
ESTERS OF PHOSPHORIC ACIDS WITH MERCURY-CONTAINING RADICALS

M. S. Malinovskii, D G. Yurko, and V. B. Tul'chinskii

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2170-2171, July, 1960
Original article submitted May 21, 1959

Mercury-containing compounds are still the most effective agents in combating bacterial and fungus diseases of plants. They are characterized by a universality of action and do not retard the germination of seed material treated with them. Our objective in the present paper was to synthesize some compounds of type (I), which, in all probability, should couple in themselves the high insecticidal activity of organophosphorus compounds and the bactericidal and fungicidal activity of organomercury compounds



To obtain these compounds we started with the dialkyl chlorophosphates, dialkyl chlorothiophosphates and o-hydroxyphenyl-mercury chloride. Condensation of the latter with the dialkyl chlorophosphates and dialkyl chlorothiophosphates was carried out in water, acetone, or benzene medium at 20–80°. Sodium hydroxide, triethylamine, pyridine and potassium carbonate were used to tie up the hydrochloric acid formed during the reaction. It proved that the condensation is best carried out in either acetone or benzene medium, in the presence of anhydrous potassium carbonate, and is ended within 6–8 hr in the cold, and within 1–2 hr at 50–80°; the yield of products is substantially lower in the latter case. The obtained compounds are given in the Table.

Formula	Found (%)			Empirical formula	Calculated (%)		
	P	S	Hg		P	S	Hg
$(C_2H_5O)_2P(O)OC_6H_4HgCl$ *	6.90	—	43.15	$C_{10}H_{14}O_4PClHg$	6.66	—	43.12
$(C_2H_5O)_2P(S)OC_6H_4HgCl$ **	6.60	6.60	41.25	$C_{10}H_{14}O_3SPClHg$	6.44	6.66	41.66
$(CH_3O)_2P(S)OC_6H_4HgCl$ ***	6.61	7.25	44.10	$C_8H_{10}O_3SPClHg$	6.83	7.07	44.25
$n\text{-}C_3H_7O)_2P(S)OC_6H_4HgCl$ ***	6.25	6.45	39.22	$C_{12}H_{18}O_3SPClHg$	6.08	6.30	39.59
$CH_3O, C_2H_5O)P(S)OC_6H_4HgCl$ ***	6.33	6.90	42.72	$C_9H_{12}O_3SPClHg$	6.63	6.86	42.93
$CH_3O, n\text{-}C_3H_7O)P(S)OC_6H_4HgCl$ ***	6.28	—	42.60	$C_{10}H_{14}O_3SPClHg$	6.44	—	42.55

*M.p. 76–77°; M 469.3, calc. 465.2 (determined by the cryoscopic method in benzene).
**M.p. 105–106°; M 485.5, calc. 481.3.
***Oil.

EXPERIMENTAL

The reaction was carried out in a three-necked flask fitted with a dropping funnel, thermometer, reflux condenser and mechanical stirrer. A charge of 32.9 g (0.1 mole) of o-hydroxyphenyl chloride, 350–400 ml of acetone and 18 g (0.13 mole) of powdered anhydrous potassium carbonate was placed in the flask. Then 12–16 ml (about 0.1 mole) of the appropriate dialkyl chlorophosphate or dialkyl chlorothiophosphate was added dropwise in 20–30 min with vigorous stirring, after which the temperature of the reaction mixture was raised to 30–40° and the mixture kept at this temperature for 2 hr with vigorous stirring, and then for another 2–4 hr in the cold without stirring. On conclusion of reaction the precipitate of mineral salts was filtered, and the acetone was distilled from the filtrate in vacuo. The residue remaining in the flask was a colorless viscous oil. O,O-Diethyl O-(2-chloromercuri) phenyl phosphate and O,O-diethyl O-(2-chloromercuri)phenyl thiophosphate were obtained in the crystalline state when the oily product was digested 3–4 times with diethyl ether. The other condensation products could not be made to crystallize and they were purified by short washing with water on the alkaline side, followed by thorough drying. The yield of the condensation products ranged from 40 to 90%. None of the products can be vacuum-distilled, and when heated above 50–130° (depending on the compound) they decompose with explosive force. The compounds are readily soluble in acetone, and somewhat less soluble in benzene. They are difficultly soluble in cold ether. When subjected to the action of water for a long time they gradually soften, probably because of hydrolysis. The pure compounds prove to be completely stable in the dry state.

SUMMARY

Six new mercury-containing organophosphorus compounds, not described in the literature, were obtained by the reaction of dialkyl chlorophosphates and dialkyl chlorothiophosphates with o-hydroxyphenylmercury chloride.

STUDY OF THE CHEMICAL STRUCTURE OF RUBBERS SKN-26 AND SKN-40 BY THE METHOD OF OZONOLYSIS

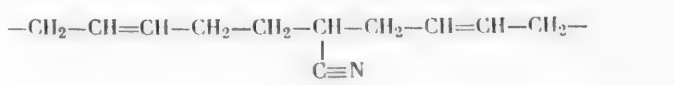
A. I. Yakubchik and A. I. Spasskova

Leningrad State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2172-2176, July, 1960
Original article submitted July 1, 1959

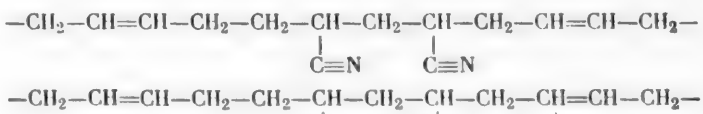
Butadiene-nitrile rubbers are obtained by the copolymerization of butadiene and acrylonitrile. Three types of butadiene-nitrile rubbers are produced by our industry: SKN-18, SKN-26 and SKN-40. The rubbers fabricated from these types possess a high benzene and oil resistance.

We used the ozonolysis method to study the structure of the commercial butadiene-nitrile rubbers SKN-26 and SKN-40. The ozonolysis of the rubbers was carried out in ethyl acetate. The ozonides were decomposed by treatment with acetyl hydroperoxide. The oxidative decomposition products of the ozonides were separated by the method of distributive chromatography, and here the following acids were found: formic, propionic, succinic, 1,2,4-butanetricarboxylic, 1,2,3-propanetricarboxylic and 1,2,4,6-hexanetetracarboxylic. The formation of these acids during ozonolysis could occur as follows: succinic acid from the 1,4−1,4 segments; formic acid from the 1,4−1,2−1,4 and 1,4−$(1,2)_2$−1,4 segments; 1,2,4- butanetricarboxylic acid from the 1,4−1,2−1,4* segments of from segment (I) [1, 2]:

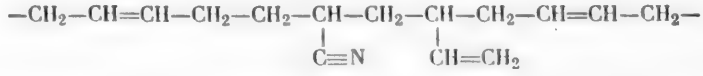


(I)

and 1,2,4,6-hexanetetracarboxylic acid from the 1,4−$(1,2)_2$−1,4* segments or from segments (II) and (III):



(II)



(III)

The 1,2,3-propanetricarboxylic acid could have been formed from the 1,4−1,4 segments, branched at the α-methylene group, or as an abnormal ozonolysis product of the 1,4−1,2−1,4 segments [3, 4]. The presence of propionic acid in the ozonolysis products indicates a profound decomposition of the carbon chain of the rubber during ozonolysis and the oxidative decomposition of the ozonide.

The amount of 1,2,4-butanetricarboxylic and 1,2,4,6-hexanetetracarboxylic acids established to be present in the ozonolysis products, is greater than could be expected on the assumption that they are formed only from the 1,4−1,2−1,4 and 1,4−$(1,2)_2$−1,4 segments. Consequently, it must be assumed that they are also formed from segments (I), (II), and (III) during ozonolysis.

* Based on a quantitative determination of the amount of HCOOH and HCHO in the ozonolysis products, it was shown that the investigated rubbers contain links with side-chain double bonds.

From the amounts of the different acids found to be present in the ozonolysis products of the investigated rubbers we calculated the fraction (in %) of the carbon skeleton of the rubbers contained in them. The results of the investigation are summarized in Table 1.

TABLE 1.

Acid	SKN-26			SKN-40		
	amount in ozonolysis products (in g)		Fraction of the carbon skeleton of the rubber in the acid, in %	amount in ozonolysis products (in g)		Fraction of the carbon skeleton of the rubber in the acid, in %
	of acid	of carbon in acid		of acid	of carbon in acid	
Propionic	0.47	0.23	3.9	0.81	0.39	3.1
Succinic	5.04	2.05	34.5	7.08	2.88	33.3
1,2,4-Butanetricarboxylic	3.62	1.60	27.0	6.76	2.99	34.5
1,2,3-Propanetricarboxylic	0.81	0.33	5.6	0.69	0.28	3.3
1,2,4,6-Hexanetetracarboxylic	0.58	0.26	4.4	0.63	0.29	3.4
Total	10.54	4.47	75.4	15.97	6.83	77.6

In rubbers SKN-26 and SKN-40 the identified acids are found to contain 75.4 and 77.6% of the carbon skeleton of the respective rubbers, while the percent of the carbon skeleton contained in those segments of the macromolecule from which the characterized acids were formed during ozonolysis is somewhat greater.* As a result, about 10–15% of the carbon skeleton of the ozonized rubbers could not be accounted for. This amount of unaccounted carbon skeleton is contained in the uncharacterized acids, which are shown as peaks I, V and X in the chromatogram (Figs. 2 and 3, Chromatogram 1), and belongs in the category of unavoidable losses during ozonolysis. From this it follows that the macromolecules of the rubbers are basically composed of segments in which the butadiene molecules are linked in the –1,4–1,4–, –1,4–1,2–1,4–and–1,4–$(1,2)_2$–1,4– positions, and segments in which either one or two acrylonitrile units are inserted between the 1,4 butadiene units (I, II).

EXPERIMENTAL

Commercial samples of butadiene-nitrile rubbers SKN-26 and SKN-40 were taken for the investigation. Rubber SKN-26 was purified from antioxidant and low-molecular fractions by dissolving it in benzene and then reprecipitating it twice from a 1% benzene solution with alcohol. Rubber SKN-40 was purified from the antioxidant by extracting it with a mixture composed of toluene and methyl alcohol. The purified rubbers were dried at 3 mm to a constant weight and then were sealed in ampuls. Both the purification and the drying of the rubbers was done in an atmosphere of dry, oxygen-free nitrogen.

The SKN-26 rubber analyzed in %: C 83.37; H 9.11; N 7.64, 7.65. The SKN-40 rubber analyzed in %: C 81.00, 80.99; H 8.70, 8.78; N 10.10, 9.90. Consequently, the acrylonitrile content of rubber SKN-26 is 28.8%, and that of rubber SKN-40 is 37.9%.

In order to determine if the nitrile group in the investigated butadiene-nitrile rubbers is attacked by ozone, we took the curves for the absorption of ozone by the rubbers. The ozonization of the rubbers was conducted in chloroform at -20°. The ozone concentration in the oxygen was 5–6%. The ozone was passed through the rubber solution at a constant rate of 7 liters per hour. The amount of ozone that added was calculated from the absorption curves (Fig. 1), which were traced at the same time that the ozonization process was run [5]. The curves for the absorption of ozone by the butadiene-nitrile rubbers do not show a break. The ozone adds at a constant rate and corresponds to the amount of ozone calculated for the double bonds –C=C– present in the rubber. The ozone added only to the double bonds in the rubber (both internal and side-chain). The nitrile groups were not attacked by the ozone. In order to establish this we took the curve for the absorption of ozone by acrylonitrile (b.p. 78–79°),

* To calculate the amount of carbon in the segments from which the acids were formed during ozonolysis is difficult, since it is not known, for example, what amount of 1,2,4-butanetricarboxylic acid was formed from the 1,4–1,2–1,4 segments and what amount from the (I) segments.

and from it we calculated the amount of added ozone (Fig. 1, Curve 1). The curve proved to be parallel to the abscissa during the entire ozonization process. The ozone added at a constant rate. From the data in Table 2 and the curve for the absorption of ozone it can be seen that the amount of added ozone corresponded only to that calculated for the double bond $-C=C-$.

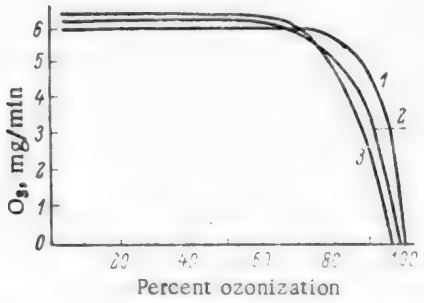


Fig. 1. Curves for the absorption of ozone. 1) Acrylonitrile; 2) rubber SKN-26; 3) rubber SKN-40.

In order to ascertain the chemical structure, the ozonization of the rubbers was run in ethyl acetate at -20°. The ozone concentration in the oxygen was 5–6%. For the ozonization we took 7.16 g of rubber SKN-26 and 10.7 g of SKN-40. The obtained ozonides were soluble in the ethyl acetate. The solvent was distilled at 20° (14 mm), after which the ozonides were dissolved in glacial acetic acid and then oxidized with acetyl hydroperoxide [4]. The acetic acid was distilled at 20° (5 mm) from the products of the oxidative decomposition of the ozonides. The decomposition products of the ozonides of the investigated rubbers represented a mixture of viscous and crystalline substances.

Decomposition products of the rubbers	Found (%)		
	C	H	N
SKN-26	41.00	7.14	4.76, 4.82
SKN-40	42.50, 42.70	6.73, 6.81	3.45, 3.53

The nitrogen content corresponds to the amount of nitrogen contained in the rubbers taken for ozonization. The SKN-26 rubber taken for ozonization contains 0.55 g of nitrogen or 2.08 g of acrylonitrile. The ozonolysis products of this rubber contain 0.51 g of nitrogen or 1.93 g of acrylonitrile. The SKN-40 rubber taken for ozonization contains 1.07 g of nitrogen or 1.93 g of acrylonitrile. The ozonolysis products of this rubber contain 0.95 g of nitrogen or 1.29 g of acrylonitrile. This indicates that the $C \equiv N$ group in the starting rubbers is not oxidized

TABLE 2.

Substance	Weight (in g)	Weight of ozone (in g)				Amount of ozone added in percent of that calculated for the double bonds in the rubber
		calculated		added		
		for double bonds in rubber	for nitrile groups in rubber	to double bonds in rubber	to nitrile groups	
SKN-26	0.55	0.355	0.136	0.347	–	97.8
SKN-40	0.55	0.312	0.162	0.309	–	97.1
Acrylonitrile	0.54	0.490	0.490	0.499	–	100.2

to acids by the ozone-containing oxygen and the acetyl hydroperoxide. For this reason the mixture of acids obtained from the oxidative decomposition of the ozonides was hydrolyzed (hydrolysis of the $C \equiv N$ groups) with sodium hydroxide, and the resulting acids were extracted with diethyl ether. We obtained 14.78 g of acids from the ozonide of rubber SKN-26 and 19.85 g of acids from the ozonide of SKN-40. The separation of these acids was effected by chromatographing on MSK silica gel (a fine silica gel with coarse pores), as described earlier [6]. By gradually changing the polarity of the mobile solvent we worked out a system of development for each mixture of acids, which enabled us to obtain a fairly distinct separation of the acids.

The chromatograms for the separation of the mixed acids obtained from the ozonolysis products of rubbers SKN-26 and SKN-40 are shown in Figs. 2 and 3. To interpret the chromatograms of the acids we took the chromatograms of a mixture of the following acids: propionic, acetic, formic, succinic, 1,2,4-butanetricarboxylic and 1,2,3-propanetricarboxylic, all of which were established earlier to be present in the ozonolysis products of butadiene and butadiene-nitrile rubbers [1, 2] (Figs. 2 and 3, Chromatogram 2). The acids were identified by the peak effluent volumes and the elution thresholds. When the chromatograms of the different acid mixtures are superimposed it can be seen that both the peak effluent volumes and the elution thresholds coincide; the order in which the acids emerge from the column is retained.

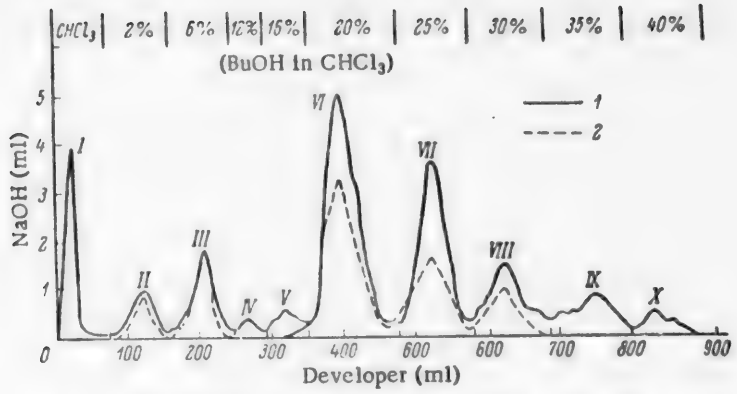


Fig. 2. Chromatograms for the separation of the mixed acids from the ozonolysis products of rubber SKN-26 (1) and of a mixture of acids (2). II) Propionic; III) acetic; IV) formic; VI) succinic; VII) 1,2,4-butanetricarboxylic; VIII) 1,2,3-propanetricarboxylic; IX) 1,2,4,6-hexanetetracarboxylic acid.*

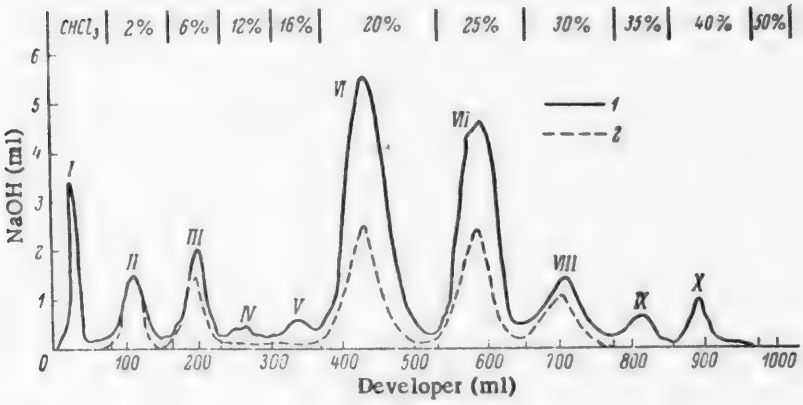


Fig. 3. Chromatograms for the separation of the mixed acids from the ozonolysis products of rubber SKN-40 (1) and a mixture of acids (2). II) Propionic; III) acetic; IV) formic; VI) succinic; VII) 1,2,4-butanetricarboxylic; VIII) 1,2,3--propanetricarboxylic; IX) 1,2,3,6-hexanetetracarboxylic acid.*

From the chromatograms for the separation of the mixed acids we calculated the amount of each acid in the ozonolysis products and the percent of the carbon skeleton of the rubbers present in the acids (Table 1). Calculation of the percent of side-chain double bonds was based on a quantitative determination of the amount of formaldehyde and formic acid [7] present in the ozonolysis products. It was determined that the amount of 1,2 links in the SKN-26 rubber is 10.8%, and 11.8% in the SKN-40 rubber.

SUMMARY

It was established that the macromolecules of the butadiene-nitrile rubbers SKN-26 and SKN-40 are built mainly from the segments 1,4—1,4; 1,4—1,2—1,4; 1,4—(—1,2—)$_2$—1,4; 1,4—CH_2—CH(C≡N)—1,4—; 1,4—(—CH_2—CH(C≡N)—)$_2$—1,4.

* The nature of the acids corresponding to peaks I, V and X was not established.

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STUDY OF THE CHEMICAL STRUCTURE OF THE SPONGY POLYMER OF ISOPRENE

A. I. Spasskova and D. I. Rabinovich

Leningrad State University
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2176-2180,
July, 1960
Original article submitted July 1, 1959

Isoprene on storage is converted to a white spongy polymer that is devoid of rubberlike properties, is insoluble in organic solvents, and shows limited swelling in them [1–3]. The spontaneous polymerization of isoprene was described in detail by S. V. Lebedev [3]. The chemical structure of the autopolymer of isoprene was studied by Harries [4]. He was able to show that both levulinaldehyde and levulinic acid are present in the ozonolysis products, and that they contain 37% of the carbon skeleton of the polymer. After removal of the levulinaldehyde and levulinic acid by distillation, it was shown by Harries that peroxide compounds are present in the residue, but he failed to establish their nature. The residue was a tarry mass.

Our objective in the present paper was to study the chemical structure of the spongy polymer of isoprene that is obtained when isoprene is polymerized in sealed ampuls, in a nitrogen atmosphere, at 15–18°. Two high-molecular polymers are formed under these conditions, one of which is rubberlike in nature and is soluble in benzene, chloroform, and other solvents, while the other polymer, representing the main bulk of the material (90–95%), is crumbly and insoluble in organic solvents; in the future the latter will be called the spongy polymer.

The chemical structure of the spongy polymer of isoprene was studied by the method of ozonolysis. The ozonide was decomposed by catalytic reduction at atmospheric pressure in dioxane solution, using palladium deposited on $BaSO_4$ as the catalyst. It was established that levulinaldehyde along with levulinic acid* are present in the catalytic reduction products, representing 63.7% of the carbon skeleton of the polymer. These two compounds are formed from those segments of the spongy polymer macromolecules in which the isoprene molecules are linked in the –1,4–1,4– positions. In addition, succinic, acetic and formic acids were found to be present in the ozonolysis products. The latter acid could have been formed during ozonolysis from the segments containing either 1,2 or 3,4 links. The paths for the formation of the succinic and acetic acids are not known: the succinic acid could have been formed from the –1,4–4,1–segments, while the acetic acid may be an abnormal ozonolysis product. In addition, the succinic and acetic acids could have also been formed as secondary products from the –1,4–1,4–segments. The presence of acetonylacetone in the catalytic reduction products of the ozonide could not be detected; for this reason it is possible to assume that a –4,1–1,4–coupling of the isoprene molecules is absent in the macromolecules of the spongy polymer of isoprene. The results of our study are given in Table 1.

By the catalytic reduction of the ozonide of the spongy polymer of isoprene at atmospheric pressure in dioxane solution, using $Pd/BaSO_4$ as the catalyst, it was established that 63.7% of the carbon skeleton of the polymer can be accounted for by a –1,4–1,4–linking of the isoprene molecules. It was also established that 14.5% of the carbon skeleton of the investigated polymer is contained in the acetic and succinic acids; to calculate the percent of the carbon skeleton of the polymer in the segments from which these acids were formed is impossible, since the paths for their formation were not elucidated.

* The catalytic reduction of ozonides is always accompanied by the side reaction of forming acids. This same reaction goes, although slowly, when the ozonide is allowed to stand [5].

TABLE 1.

Ozonolysis products	Weight (in g)	Structure of segment from which the compound was formed	Percent of carbon skeleton in the compound
Levulinaldehyde	2.97	—1,4—1,4—	40.9
Levulinic acid	1.92	—1,4—1,4—	22.8
Acetic acid	0.96	Either abnormal ozonolysis product or secondary product from the—1,4——1,4—segment	8.9
Succinic acid	0.60	Either from—1,4—4,1—or from—1,4——1,4—, as secondary product	5.5
Formic acid	0.02	Either 1,2 or 3,4 link	0.1
Residue	1.02	—	14.0
Total	7.49	—	92.2

EXPERIMENTAL

The autopolymer of isoprene was obtained by the spontaneous polymerization of isoprene in sealed ampuls at 15—18° with illumination, in a nitrogen atmosphere. The isoprene taken for polymerization had b.p. 34.2—34.5° and n_D^{20} 1.4152. Extraction of 38 g of the isoprene autopolymer with chloroform gave us 4.2 g (11%) of the rubbery polymer. The remainder was the spongy polymer, a white crumbly substance, devoid of elastic properties and insoluble in organic solvents.

Found %: C 87.06, 87.24; H 11,77, 11.69. $(C_5H_8)_x$. Calculated %: C 88.24; H 11.76.

The ozonization of the spongy polymer of isoprene was run in chloroform at -30° using oxygen that contained 5—6% of ozone, in an apparatus that made it possible to maintain a constant ozone concentration [6]. The polymer was ozonized in 2 g portions. The addition of the ozone went at a constant rate and corresponded to the addition of 1.45 moles of ozone, or 103% of that calculated for the double bonds in the polymer. The amount of added ozone was calculated from the absorption curves, which were traced at the same time that the ozonization process was run. The spongy polymer of isoprene is ozonized completely in chloroform, forming a clear, colorless solution of the ozonide. Removal of the chloroform leaves the ozonide as a viscous colorless substance. The ozonide was decomposed by catalytic reduction at atmospheric pressure in dioxane solution, using $Pd/BaSO_4$ as the catalyst.

Five grams of the spongy polymer of isoprene was ozonized in chloroform (containing 4.4 g of the hydrocarbon). We obtained 8.61 g of the ozonide. The ozonide was dissolved in dioxane (b.p. 101°, n_D^{20} 1.4215, d^4_{20} 1.0336; the test for the presence of peroxides was negative). The catalytic reduction of the ozonide was run in a S. V. Lebedev apparatus [7]. We took 1.5 g of $Pd/BaSO_4$ catalyst [8] to reduce 1 g of the ozonized polymer.

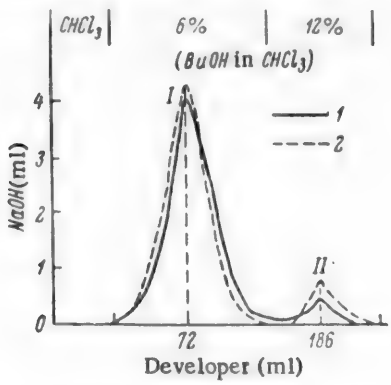

Fig. 1. Chromatograms for the separation of the mixed acids present in the dioxane distilled from the products obtained in the catalytic reduction of the ozonide of the spongy polymer of isoprene (1), and of a mixture of acetic and formic acids (2). I) Acetic acid; II) formic acid.

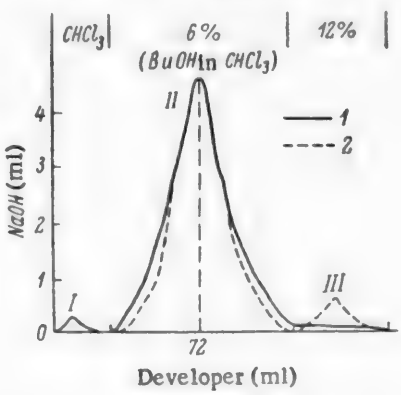

Fig. 2. Chromatograms for the separation of the mixed acids in the 1st fraction (1) and of a mixture of acetic and formic acids (2). II) Acetic acid; III) formic acid.

Fischer states that the catalytic reduction of ozonides with the indicated catalyst goes to the formation of carbonyl compounds [5]. At 5° (760 mm) the amount of hydrogen consumed in the reduction of the ozonide was 906 ml (889 ml at 0° and 760 mm), which corresponds to 54% of the calculated. A possible explanation of this is that a partial decomposition of the ozonide occurs during ozonization and when distilling the solvent from the ozonide. A solution of the catalytic reduction products of the ozonide gave a negative test for peroxides and ozonides. The dioxane was distilled from the hydrogenation products of the ozonide at 25° (10 mm). The distilled dioxane was acid to litmus (0.8 ml of 0.1N KOH was required to neutralize 1 ml of the dioxane). The separation of the acids contained in the distilled dioxane was done chromatographically on MSK silica gel (a fine silica gel with coarse pores), as described earlier [9]. The chromatogram for the mixture of acids present in the dioxane distilled from the products obtained in the catalytic reduction of the ozonide of the investigated polymer is shown in Fig. 1. To interpret the obtained chromatogram, we took the chromatogram of a mixture of acetic and formic acids (Fig. 1, Chromatogram 2). The acids were identified by the peak effluent volumes (Table 2) [10]. When the chromatogram of acetic acid and formic acid is superimposed on the chromatogram of the acids isolated from the dioxane it can be seen that the peak effluent volumes of the acids coincide; the order in which the acids emerge from the column is retained.

TABLE 2.

Mixture of acids being separated	Peak effluent volumes of the acids	
	acetic acid	formic acid
Acids isolated from the dioxane	72	186
Mixture of acids	72	186

TABLE 3.

Mixture of acids being separated	Peak effluent volumes of the acids	
	levulinic acid	succinic acid
Acids from the residue	69	240
Mixture of levulinic and succinic acids	69	240

The amounts of acetic and formic acids were calculated from the chromatogram: acetic 0.32 g, and formic 0.02 g.

We took 18 g of the products obtained from the catalytic reduction of the ozonide of the spongy isoprene polymer and fractionated the material through a column. The following fractions were collected: 1st, b.p. 30–35° (10 mm), 11.47 g; 2nd, b.p. 62–63° (10 mm), 2.97 g; residue, 3.54 g. The 1st fraction was acid to litmus and had a strong odor of acetic acid (14.5 ml of 0.1N KOH was consumed in the neutralization of 1 ml); in addition, this fraction also contained dioxane. We took the chromatogram of the mixture of acids contained in the 1st fraction. The chromatograms for the separation of the mixed acids contained in the 1st fraction and of a mixture of formic and acetic acids are shown in Fig. 2. From Chromatogram 1 (Fig. 2) it can be seen that the 1st fraction contains mainly acetic acid. The amount of acid contained in the 1st fraction was calculated from the chromatogram and found to be equal to 0.64 g. The 2nd fraction was levulinaldehyde, b.p. 62–63° at 10 mm, $n_D^{21.5}$ 1.4254. The p-nitrophenylhydrazone of levulinaldehyde was prepared, m.p. 104–104.5°.*

The residue from the fractional distillation of the products obtained in the catalytic reduction of the ozonide of the spongy isoprene polymer was subjected to chromatographic separation, and was shown to contain both levulinic and succinic acids. The chromatograms for the separation of the residue (Chromatogram 1) and of a mixture of levulinic and succinic acids, the latter (Chromatogram 2) taken for the purpose of identifying the acids present in the residue, are shown in Fig. 3. The acids, isolated from the residue, were identified by the peak effluent volumes (Table 3).

The amounts of levulinic and succinic acids were calculated from the chromatogram: they are respectively equal to 1.92 and 0.6 g.

The chromatographic characterization of levulinic acid was confirmed by the chemical analysis data. For this we collected the peak effluent volume corresponding to the levulinic acid. The chloroform and butyl alcohol were removed by distillation from the isolated substance.

Found %: Ag 48.31, 47.98. $C_5H_7O_3Ag$. Calculated %: Ag 48.19.

*From [11]: b.p. 70° (12 mm), $n_D^{21.5}$ 1.4256; p-nitrophenylhydrazone, m.p. approximately 106°.

The 2,4-dinitrophenylhydrazone of levulinic acid was prepared, m.p. 205–205.5° [12].

The residue remaining after isolation of the levulinic and succinic acids was a tarry material, weighing 1.02 g (% C 61.00, 61.30; % H 8.32, 8.19). From the elemental analysis we calculated the percent of the carbon skeleton of the polymer present in the residue (14%).

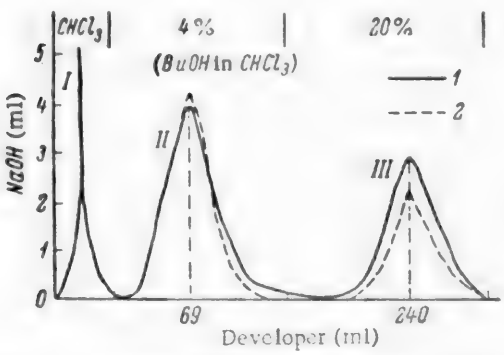

Fig. 3. Chromatograms for the separation of the residue from the fractional distillation of the products obtained in the catalytic reduction of the ozonide of the spongy isoprene polymer (1), and of a mixture of levulinic and succinic acids (2). II) Levulinic acid; III) succinic acid.

Based on a quantitative determination of the amounts of levulinic, succinic, acetic and formic acids and of levulinaldehyde present in the products of the catalytic decomposition of the ozonide of the spongy isoprene polymer it was shown that the amount of the carbon skeleton contained in them as a whole is 78.2% (Table 1).

SUMMARY

1. Analysis of the products obtained in the ozonolysis of the spongy polymer of isoprene reveals that 63.7% of the carbon skeleton of the polymer exists as −1,4−1,4− linkages.

2. It was shown that the acetic and succinic acids which appear as secondary products of the −1,4−1,4− segments contain 14.5% of the carbon skeleton of the spongy isoprene polymer.

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*Original Russian pagination. See C. B. translation.

THE SYNTHESIS OF AMIDES AND THEIR HYDROCHLORIDES FROM NITRILES

A. E. Kulikova, E. N. Zil'berman, and N. A. Sazanova

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2180-2183,
July, 1960
Original article submitted June 29, 1959

Methods are described in the literature for the hydrolysis of nitriles to amides using hydrogen peroxide in alkaline medium [1], and also concentrated sulfuric [2] and hydrochloric [3] acids. Recently, schemes have been proposed for the synthesis of amides based on hydrolyzing nitriles in the presence of either polyphosphoric acid [4] or a mixture of acetic acid and boron trifluoride [5]. It was shown by us recently [6, 7] that adiponitrile, capronitrile and benzonitrile, when treated with water and hydrogen chloride in the cold in organic solvents, are converted, apparently through the chlorides of the imonium chlorides (I), to the hydrochlorides of the amides, the structural formula of which corresponds to the chlorides of the imoniumhydrins of the carboxylic acids (II). Treatment of the amide hydrochlorides with excess water gave the corresponding amides. The scheme proposed by us for the synthesis of amide hydrochlorides proceeds under mild conditions and is a convenient method for the preparation of both amides and their hydrochlorides. In addition, the given method makes it possible to obtain amides from nitriles containing reactive functional groups in the molecule.

$$RCN + 2HCl \underset{(a)}{\rightleftarrows} \underset{(I)}{\left[RC\begin{matrix}NH_2\\Cl\end{matrix}\right]^+Cl^-} \xrightarrow[(b)]{H_2O} \underset{(II)}{\left[RC\begin{matrix}NH_2\\OH\end{matrix}\right]^+Cl^-} \xrightarrow{H_2O} RC\begin{matrix}O\\NH_2\end{matrix}$$

It should be mentioned that earlier Pinner [8] had also apparently obtained the imoniumhydrin chlorides by passing hydrogen chloride through ether solutions containing water and acetonitrile or benzonitrile, but he failed to give any details regarding the properties, structure and yields of the compounds.

In order to determine to what extent the method proposed by us earlier [6, 7] for the preparation of amides and their hydrochlorides is general, we investigated in the present paper the reaction of the aliphatic nitriles: aceto-, chloroaceto-, trichloroaceto-, phenylaceto-, β-chloropropio-, β-ethoxypropio-, capro- and stearonitriles, and also of the methyl ester of δ-cyanovaleric acid and of azobisisobutyronitrile, as well as a member of the aromatic series, namely benzonitrile, with hydrogen chloride and water (see Table). The hydrochlorides of β-chloropropionamide, phenylacetamide, stearamide, and of the methyl ester of adipamic acid, and also the methyl ester of adipamic acid, are new compounds. The hydrochloride of caproamide was not isolated since it proved to be very unstable in the air. The hydration of chloroacetonitrile gave a mixture of chloroacetamide and its hydrochloride. Only the free amide is formed in the case of trichloroacetonitrile.

The experiments in the table are arranged in the order of decreasing reactivity of the nitriles. Attention is attracted to the fact that, as a rule, the presence of an electronegative substituent in the nitrile accelerates the formation of amide hydrochlorides, while a positive substituent retards such formation. However, deviations from the general rule exist; for example, under the same conditions the yield of amide was greater from stearonitrile than from capronitrile. Of the investigated compounds, only β-ethoxypropionitrile and azobisisobutyronitrile fail to hydrolyze to the corresponding amides.

Starting nitrile	Time of crystallization (days)	Imoniumhydrin chloride (II)							Amide	
		Yield (%)	Melting point (with decompn.)	Found (%)		Empirical formula	Calculated (%)		Yield (in % on nitrile)	Melting point
				Cl^-	N		Cl^-	N		
Chloroacetonitrile	0.7	–	–	–	–	–	–	–	90	121–122*
Trichloroacetonitrile	0.7	–	–	–	–	–	–	–	94	141–142
β-Chloropropionitrile	1	95	50–60*	24.0	10.1	$C_3H_7ONCl_2$	24.5	9.8	86	102–104*
Phenylacetonitrile	2	91	113–117	20.8	8.2	$C_8H_{10}ONCl$	20.7	8.1	88	156–158
Acetonitrile	1	92	142	37.1	14.6	C_2H_6ONCl	37.1	14.7	85	845
Benzonitrile	3	96	68	22.6	9.4	C_7H_8ONCl	22.6	9.5	95	125
Stearonitrile	7	87	85	11.4	4.0	$C_{17}H_{36}ONCl$	11.1	4.3	87	108
Capronitrile	7	–	–	–	–	–	–	–	73	100
Methyl ester of δ-cyanovaleric acid	5	52	156–158	18.2	7.4	$C_7H_{14}O_3NCl$	18.2	7.2	30	92

* According to [9]: m.p. 101-102°.

The formation of amide hydrochlorides from nitriles and water in the presence of hydrogen chloride can go in other solvents (benzene, toluene, dioxane, etc.) besides ether [6], and also without a solvent. However, of the different solvents it proved that ether, as a rule, was the best. An excess of hydrogen chloride exerts a noticeable accelerating effect on the hydration rate of the nitriles, since the first stage of the synthesis (a) is a reversible process and an excess of hydrogen chloride shifts the equilibrium toward the chloride of the imonium chloride (I). It should be mentione that if it is desired to synthesize the free amide, then there is no need to isolate the imoniumhydrin chloride from the reaction medium. In the case of reactive nitriles the synthesis of the imoniumhydrin chlorides (II) is best accomplished with cooling. It proved that with the less reactive nitriles (benzonitrile, stearonitrile and capronitrile) the reaction was best carried out at room temperature.

In a previous paper [6] it was shown indirectly that the products obtained in the reaction of nitriles with hydrogen chloride, taken in an equivalent ratio of 1 : 2, apparently being chlorides of the imonium chlorides (I), are intermediate products in the synthesis of the imoniumhydrin chlorides (II). However, statements exist [10, 11] in the literature that such substances (I) when treated with water can decompose only to the starting nitriles and hydrogen chloride. To obtain experimental proof of the conclusion made by us earlier, in the present study we isolated the chloride of acetimonium chloride (I, R = CH_3) from the reaction products of acetonitrile with hydrogen chloride and then treated the substance with an equivalent amount of water in the cold. Here the acetimoniumhydrin chloride (II, R = CH_3) was obtained in high yield. The erroneous reasoning in the papers by Hantzsch [10] and Hinkel [11] was due to the fact that they treated (I) with a large excess of water, which caused the equilibrium of reaction (a) to shift to the left, whereas in the method proposed by us for the preparation of amide hydrochlorides (II) the water reacts only in accordance with reaction (b). At the same time, our data do not exclude the possibility of a different mechanism for the conversion of nitriles to amide hydrochlorides and amides. It is entirely probable, for example, that in the case of reactive nitriles (trichloroacetonitrile, etc.), and also when the reaction is run under comparatively drastic conditions, the hydrogen chloride fails to form stable imoniumchloride chlorides or other saltlike compounds with the nitriles, and instead functions as a catalyst for the reaction [12].

EXPERIMENTAL

The starting nitriles used in our work were anhydrous compounds, with constants corresponding to those reported in the literature.

Acetamide and its hydrochloride. The saturation of 8.2 g of acetonitrile in 10 ml of ether with dry hydrogen chloride [11] gave 22.2 g (97%) of the chloride of acetimonium chloride (I, R = CH_3), m.p. 6°. With stirring and cooling to 0°, a suspension of 11.4 g of (I) in 10 ml of dry ether was treated with 1.8 ml of water. After 4 days the white precipitate was filtered, followed by washing with ether and drying to constant weight in a vacuum-desiccator. We obtained 8.8 g (92%) of acetimoniumhydrin chloride, m.p. 142° (decompn.); the mixed melting point with the hydrochloride obtained from acetamide [13] was not depressed. The saturation of an ether solution of 4.1 g of acetonitrile and 1.8 g of water with 37 g of hydrogen chloride, followed by standing for a day, gave 8.8 g of acetamide hydrochloride. The same substance (II, R = CH_3) was obtained in 93% yield from the same starting materials, but omitting the solvent, by heating at 50° for 6 hr. Operating as described earlier [6], we isolated 1.35 g (93%) of acetamide from 2.45 g of acetimoniumhydrin chloride.

Methyl ester of adipamic acid and its hydrochloride. Saturation of a solution of 14.1 g of methyl δ-cyanovalerate [14] and 1.8 g of water in 30 ml of dry ether with 40 g of dry hydrogen chloride at 0–5° gave after 5 days 9.8 g (51%) of the hydrochloride of methyl adipamate [II, R = $CH_3OOC(CH_2)_4$]. The product softens at 110° and melts at 156–158° (decompn.).

A solution of 3.7 g of methyl adipamate hydrochloride in 20 ml of water was neutralized with sodium carbonate to methyl orange. The obtained amide was extracted with ethyl acetate. The extract was dried over anhydrous Na_2SO_4, after which the solvent was removed to yield 1.7 g (57%) of methyl adipamate, m.p. 92–93° (from a mixture of ethyl acetate and ether).

Found %: C 52.72; H 8.27; N 8.66. $C_7H_{13}O_3N$. Calculated %: C 52.83; H 8.17; N 8.80.

Conversion of the other nitriles to the corresponding amide chlorides was accomplished in the same manner as the preparation of the hydrochloride of methyl adipamate, i.e., by saturating ether solutions of the nitriles and water at 0–5° or at room temperature (benzonitrile) with a 3–5 fold excess of hydrogen chloride. The hydrochlorides of caproamide and stearamide were obtained in the toluene medium at 20°. In all of the

experiments the imonium hydrin chlorides (II) were worked up when a substantial increase in the amount of precipitate in the reaction mixture was no longer observed. The isolation of the amides and their hydrochlorides was done in the same manner as the isolation of δ-cyanovaleramide [6]. The yields and the constants of both the amides and their hydrochlorides are given in the Table.

SUMMARY

1. It was shown that the earlier described reaction of nitriles with hydrogen chloride and water represents a convenient method for the preparation of amides and their hydrochlorides.

2. It was shown that for the most part electronegative substituents in the starting nitriles facilitate a progress of the reaction.

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SOME NEW DERIVATIVES OF THIOUREA

FUROYL- AND BENZOYLTHIOUREA

I. G. Gakh and Z. N. Nazarova

Rostov-on-Don State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2183-2186,
July, 1960
Original article submitted July 15, 1959

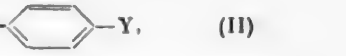
In recent years different thiourea derivatives have attracted the attention of many investigators because of their physiological activity [1]. A large number of all kinds of thiourea derivatives, many of which exhibit substantial antitubercular activity, have been synthesized and subjected to biological testing. A number of authors [2] have made attempts to elucidate the mechanism of the action of these compounds on microorganisms, and also the relationship between the structure of thiourea derivatives of type R—NH—CS—NH—R' (I) and their tuberculostatic activity.

When compounds of type (I) were tested it was found that the greatest activity is possessed by those thiourea derivatives in which R = p-C_6H_4X, where X = Cl, Br, I, F, alkyl or alkoxy group (from C_2 to C_5), and R' = p-C_6H_4Y, where Y = Cl, Br, I, F, alkyl, alkoxy, dialkylamino, ethoxydialkylamino, sulfonamido, and other groups, or pyridyl, piperidyl, naphthyl, 2-thiazolyl, dimethylisoxazolyl, sulfathiazolyl, and other groups.

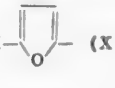
It is assumed that the mechanism of the action of thiourea derivatives on microorganisms is linked with their complex-formation ability, since all of these derivatives are capable of giving complexes with heavy metal salts [3].

Thiourea derivatives containing the aroyl radical (I, R = XC_6H_4CO) have received little study as yet. Some [4] N-aroyl-N'-aryl-substituted thioureas (I, R = phenyl, p-nitrophenyl, p-dimethylaminophenyl; R' = p-tolyl, p-ethoxyphenyl, p-nitrophenyl) have been synthesized, and also [5] compounds of type p-$O_2NC_6H_4$ CONHCSNHR, where R = p-C_6H_4Cl, p-C_6H_4Br, p-C_6H_4I, 2-pyridyl, 2-thiazolyl, or isonicotinoylamido group. The testing of these derivatives revealed that they completely inhibit the growth of tubercle bacillus at a concentration of 10^{-5} mg/liter. Thiourea derivatives containing the furoyl radical have remained completely unstudied.

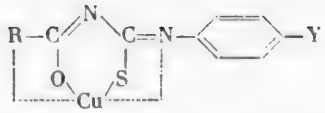
In order to fill in the indicated gap and to trace the effect of introducing the furan ring on the change in the activity and toxicity of thiourea derivatives we undertook the task of synthesizing some new N-benzoyl-, N--furoyl- and N-5-halofuroylcarbanilides of general formula



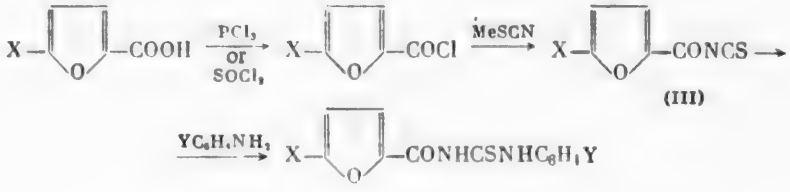
(II)

where: R = X—  (X = H, Br), C_6H_5, Y = CH_3, CH_3O, Cl.

In addition to their pharmacological interest, these compounds could be of interest in analytical chemistry [6] as active complexing agents.



We obtained both the benzoyl and the furoyl derivatives by heating the appropriate acid chloride with either sodium or ammonium thiocyanate in anhydrous acetone and subsequent condensation with amines [7].

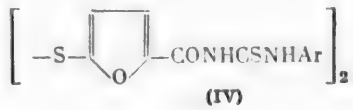


(III)

The benzoyl and furoyl isothiocyanates (III), obtained here as intermediate products, can be isolated in the free state. They are colorless liquids that tend to solidify 10–15° above the corresponding acid chloride.

The known tolylthiourea with m.p. 188° was obtained when the 1-benzoyl-3-p-tolyl- and 1-furoyl-3-p-tolylthioureas were refluxed with 10% caustic.

Depending on the conditions, in the preparation of the 5-bromofuroyl derivatives of thiourea either the 1-(5-bromofuroyl)-3-arylthiourea or the corresponding disulfide (IV) is obtained.



(IV)

The formation of the disulfide could occur as the result of replacing the bromine in the furan ring by the thiocyanate radical at the start of reaction, because of the presence of excess NH_4SCN, and subsequent conversion of the thiocyanate derivative to the disulfide.

EXPERIMENTAL

Preparation of 2-furoyl chloride.* A charge of 11.1 g (0.1 mole) of recrystallized and dried 2-furoic acid was placed in a 100-ml round-bottomed flask, fitted with a reflux condenser that was protected by a $CaCl_2$ tube. Then 8 g (0.06 g mole) of PCl_3 was added and the flask was heated on the water bath for 4 hr. The obtained black liquid was decanted from the precipitate and vacuum-distilled; b.p. 72° (25 mm). Yield 7.5 g (66%).

General procedure for the preparation of N, N'-derivatives of thiourea. An equimolar amount of either sodium or ammonium thiocyanate was dissolved in anhydrous acetone and added to the acid chloride. After heating on the water bath for 10 min, an equimolar amount of the amine in anhydrous acetone was added. The reaction mixture was heated for 15 min, then cooled, filtered, and washed with water (to remove thiocyanate) and then with cold alcohol (to remove the amine). Yield 40–70%. The product was recrystallized twice from acetone (or from a mixture of alcohol and acetone, or from glacial acetic acid).

All of the synthesized thiourea derivatives are solids, soluble in hot acetone, alcohol, and glacial acetic acid. They crystallize as either white or yellow-green needles. The obtained compounds are listed in the Table.

Preparation of disulfide (IV). A solution of 3.13 g (0.015 mole) of 5-bromo-2-furoyl chloride* and 1.14 g (0.015 mole) of NH_4SCN in 5 ml of anhydrous acetone was refluxed for several minutes. A solution of 1.85 g (0.015 mole) of anisidine in 5 ml of anhydrous acetone was then added to the reddish-orange mass. The reaction mixture was refluxed for about 1 hour, and then it was poured into 25 ml of water. Here a dark red oil was obtained, which crystallized on cooling. The crystals were filtered and washed with alcohol. This gave a yellow compound,

*By analogy with the preparation of benzoyl chloride [8].

*5-Bromo-2-furoyl chloride was obtained by the procedure given in [9].

N,N'-Derivatives of Thiourea Compound	Properties	Melting point	Recrystallized from:	Empirical formula	% N	
					Found	Calculated
1-Benzoyl-3-p-tolylthiourea	White needles, soluble in ether and hot acetone, insoluble in alcohol	156–157°	Acetone	$C_{15}H_{14}ON_2S$	10.46	10.37
1-Benzoyl-3-p-anisylthiourea	White needles, soluble in hot acetone and alcohol	146–147	Alcohol and acetone	$C_{15}H_{14}O_2N_2S$	9.90	9.78
1-Furoyl-3-p-tolylthiourea	White crystals, soluble in cold acetone	124–125	Alcohol	$C_{13}H_{12}O_2N_2S$	10.81	10.77
1-Furoyl-3-p-anisylthiourea	Yellow-green crystals, soluble in hot alcohol	114–115	Alcohol	$C_{13}H_{12}O_3N_2S$	10.26	10.15
1-Furoyl-3-p-chlorophenylthiourea	Yellow needles, soluble in hot alcohol, acetone, and hot glacial acetic acid	128–129	Acetic acid and alcohol	$C_{12}H_9O_2N_2SCl$	10.06	9.93
1-(5-Bromofuroyl)-3-p-anisylthiourea	Yellow-green crystals, soluble in hot acetone	141–142	Acetone	$C_{13}H_{11}O_3N_2SBr$	8.01	7.88
1-(5-Bromofuroyl)-3-p--chlorophenylthiourea	Yellow crystals, soluble in hot acetone	164–165	Acetone	$C_{12}H_8O_2N_2SBrCl$	8.35	7.79

containing both sulfur and nitrogen. After two recrystallizations from alcohol the compound had m.p. 135–136°.

Found %: N 8.73, 8.73. $C_{28}H_{22}O_6N_4S_4$. Calculated %: N 9.12.

SUMMARY

1. A number of new N-aroyl (benzoyl, furoyl, 5-bromofuroyl)-N'-aryl-substituted derivatives of thiourea were obtained by reacting the proper acid chlorides with metal thiocyanates and subsequent condensation with aromatic amines (p-toluidine, p-anisidine, p-chloroaniline).

2. Depending on the reaction conditions, it was shown that it is possible for 5-bromo-2-furoyl chloride to react with ammonium thiocyanate in two ways: with only the chlorine atom reacting or with both the chlorine and the bromine atoms reacting simultaneously.

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*Original Russian pagination. See C. B. translation.

CHEMISTRY OF 2,1,3-THIADIAZOLE

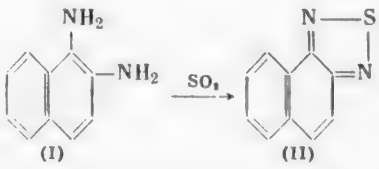
XI. CHLORINATION AND BROMINATION OF 1',2'-NAPHTHO-2,1,3-THIADIAZOLE

V. G. Pesin, A. M. Khaletskii, and L. A. Kaukhova

Leningrad Chemical-Pharmaceutical Institute

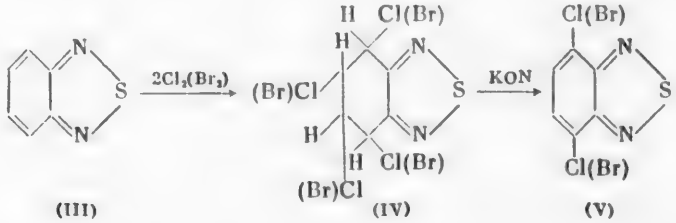
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2187-2192, July, 1960
Original article submitted July 11, 1959

1',2'-Naphtho-2,1,3-thiadiazole (II) was obtained for the first time by heating 1,2-naphthalenediamine (I) with sulfur dioxide at 180–200° for 8 hr [1].

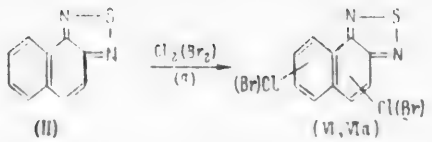


Despite the lapse of 70 years since the compound was first synthesized, this heterocycle has remained completely unstudied, possibly because a convenient method for its synthesis fails to exist. Earlier we had shown that compound (II) can be easily obtained by reacting (I) with thionyl chloride in the presence of tertiary bases (pyridine, triethylamine), or with thionylaniline. Subsequently it was established by us that thionylaniline reacts readily not only with 1,2-naphthalenediamine, but also with its salts, to give (II) in 95% yield [2].

In previous investigations we had also established that benzo-2,1,3-thiadiazole (III) and many of its derivatives exhibit a distinct aromatic character in their more important chemical properties and that (III) possesses definite unsaturation. Thus, for example, (III) readily reacts with either chlorine or bromine to add four halogen atoms and respectively yield the tetrachloro- or the tetrabromotetrahydrobenzo-2,1,3-thiadiazole (IV), which when treated with alcoholic KOH solution are converted to 4,7-dichloro- and 4,7-dibromobenzo-2,1,3-thiadiazole (V), respectively.

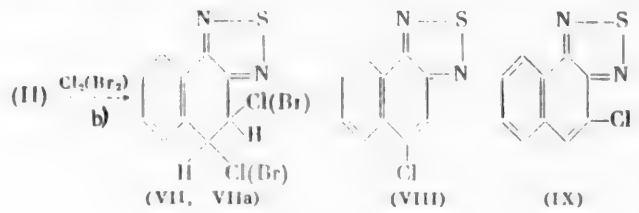


As a result, depending on the conditions, when chlorine or bromine is reacted with 1',2'-naphtho-2,1,3-thiadiazole it is possible for the reaction to go in several directions: the halogen replaces hydrogen in only one or in both rings (VI, VIa), as shown by Scheme (a).

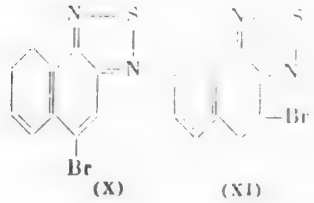


(II) (VI, VIa)

If the halogens add it is possible to expect the introduction of two atoms with the formation of the dichloro- and dibromodihydro-1',2'-naphtho-2,1,3-thiadiazoles (VII, VIIa), respectively, in accordance with Scheme (b).



(VII, VIIa) (VIII) (IX)

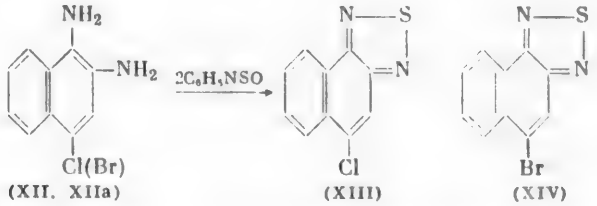


(X) (XI)

It was established by us that 1',2'-naphtho-2,1,3-thiadiazole reacts readily with either chlorine or bromine in hot glacial acetic acid with the respective formation of the dichloro- or dibromo derivatives of 1',2'-naphtho--2,1,3-thiadiazole (VI, VIa), which do not react with alcoholic caustic solution under the usual conditions (with the cleavage of either hydrogen chloride or hydrogen bromide); consequently, under the indicated conditions the substitution goes in accordance with Scheme (a). Changing the reaction conditions in order to obtain the monochloro or monobromo derivatives of 1',2'-naphtho-2,1,3-thiadiazole gave negative results. Thus, at 15° and lower, independent of the amount of bromine present, only the dibromo derivative (VI) is formed, and a part of (II) remains unreacted when 1 mole of bromine is used.

The reaction of either chlorine or bromine with 1',2'-naphtho-2,1,3-thiadiazole in the molten state results in the addition of two halogen atoms with the respective formation of the dichloro- or dibromodihydro-1',2'--naphtho-2,1,3-thiadiazoles (VII, VIIa), which when treated with alcoholic KOH solution are converted respectively to the 4'-chloro (VIII) and a mixture of the 4'- and 3'-bromo derivatives of 1',2'-naphtho-2,1,3-thiadiazole (X, XI), in accordance with Scheme (b).

We proved the structure of the halo derivatives by comparing their properties with the properties of the 4'--chloro- and 4'-bromo-1',2'-naphtho-2,1,3-thiadiazoles (XIII, XIV) that were synthesized by reacting the corresponding o-naphthalenediamines (XII) with thionylaniline in accordance with the reaction.

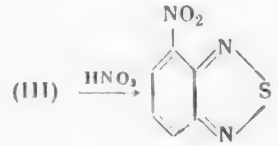


(XII, XIIa) (XIII) (XIV)

Compound (VIII), formed by the reaction of alcoholic caustic solution with (VII), proved to be identical with (XIII), which was obtained from 4-chloro-1,2-naphthalenediamine (XII); the mixed melting point of (VIII) and (XIII) was not depressed. Judging from the melting point (113–124°), the substance formed when (VII) is re-

acted with alcoholic caustic is most probably a mixture of (X) and (XI). The bromo derivative (XIV), obtained by the reaction of 4-bromo-1,2-naphthalenediamine (XIIa) with thionylaniline, melts at 124–125°; a mixture of (XIV) and (X + XI) melts at 107–113°, i.e., at a temperature that is close to the lower limit of the melting points of (X) and (XI).

According to the literature [2], replacement of hydrogen in benzo-2,1,3-thiadiazole (III) is determined chiefly by the substituent present in the aromatic ring, and not by the thiadiazole ring. Entrance of the chlorine atom in the 4' position is in harmony with these conclusions, since it is possible to regard 1',2'-naphtho-2,1,3--thiadiazole as being benzo-2,1,3-thiadiazole, substituted in positions 6 and 7. On the other hand, the fact that bromine enters both the 4' and 3' positions indicates that the thiadiazole ring exerts a definite influence in the given reaction (cleavage of hydrogen halide from compounds VII and VIIa), favoring substitution in the 3' position, similar to the situation that exists in the nitration and sulfonation of benzo-2,1,3-thiadiazole (III); in these reactions, as is known, the nitro group and likewise the sulfo group enter the 4 position.



The starting 1,2-naphthalenediamine and its 4-chloro and 4-bromo derivatives were obtained partly as described in the literature [8–12] and partly by improved procedures, as described in EXPERIMENTAL.

EXPERIMENTAL

3',4'-Dichlorodihydro-1',2'-naphtho-2,1,3-thiadiazole (VII). Molten 1',2'-naphtho-2,1,3-thiadiazole (II) (3.2 g), m.p. 81°, was saturated at 100° with chlorine (the reaction went with the evolution of heat); we obtained 4.45 g of the compound, m.p. 153–153.5° (from alcohol).

Found %: N 10.32, 10.51; S 12.36, 12.60. $C_{10}H_6N_2SCl_2$. Calculated %: N 10.89; 12.45.

4'-Chloro-1',2'-naphtho-2,1,3-thiadiazole (VIII). a) A mixture of 1 g of 3', 4'-dichlorodihydro-1',2'-naphtho-2,1,3-thiadiazole, 35 ml of alcohol and 0.6 ml of 40% NaOH solution was heated at the boil for 1 hr, then the reaction mixture was diluted with 35 ml of water, the whole was then heated at the boil for 15 min, and after cooling, the precipitate was filtered and washed with aqueous alcohol; we obtained 0.75 g of white substance, which after recrystallization from dilute alcohol had m.p. 124°. The mixed melting point with authentic 4'-chloro--1',2'-naphtho-2,1,3-thiadiazole was not depressed.

Found %: N 12.16, 12.22; S 14.94, 15.17. $C_{10}H_5N_2SCl$. Calculated %: N 12.64; S 14.45.

b) A mixture of 2.6 g of 4-chloro-1,2-naphthalenediamine, m.p. 124°, and 2.2 ml of thionylaniline in 20 ml of pyridine was heated for 1 hr on the boiling water bath, then cooled, and the solution treated with 4% hydrochloric acid until acid. The obtained precipitate was filtered, washed with water until neutral, and then recrystallized from alcohol (using carbon); m.p. 122–124°.

Found %: N 12.34, 12.656; Cl 16.21, 16.19. $C_{10}H_5N_2SCl$. Calculated %: N 12.69; Cl 16.10.

3',4'-Dibromodihydro-1',2'-naphtho-2,1,3-thiadiazole (VIIa). Bromine (2 ml) was added to 4 g of molten 1',2'-naphtho-2,1,3-thiadiazole, after which the mixture was heated for 1 hr up to the boil, then cooled, and the excess bromine was evaporated. We obtained 7.3 g of substance, which after recrystallization from acetone had m.p. 210°.

Found %: N 8.25, 8.09; Br 46.65, 46.46. $C_{10}H_6N_2SBr_2$. Calculated %: N 8.09; Br 46.24.

Mixture of 3'-and 4'-bromo-1',2'-naphtho-2,1,3-thiadiazoles (X, XI). A mixture of 1.5 g of 3',4'-dibromodihydro-1',2'-naphtho-2,1,3-thiadiazole (VIIa), m.p. 210°, 50 ml of alcohol and a solution of 0.3 g of KOH in 0.6 ml of water was heated for 2 hr at the boil, after which the reaction mixture was diluted with water. After cooling, the precipitate was filtered and washed in succession with water and dilute alcohol. Here we obtained 1.15 g of substance with a vague melting point, which was heated in boiling alcohol for 30 min and then filtered

hot to give 0.25 g of insoluble substance with m.p. 187–197°. The hot filtrate was treated with small portions of water until a turbidity appeared, which was made to disappear by the addition of a little alcohol, after which the clear solution was cooled and the obtained precipitate filtered and washed with aqueous alcohol; we obtained 0.51 g of crystalline compound with m.p. 100–122°. After recrystallization from alcohol (using carbon), m.p. 113–124°. A mixture of the compound with authentic 4'-bromo-1',2'-naphtho-2,1,3-thiadiazole melted at 107–113°.

Found %: N 10.56, 10.28; Br 30.42, 30.23. $C_{10}H_5N_2SBr$. Calculated %: N 10.56; Br 30.19.

4'-Bromo-1',2'-naphtho-2,1,3-thiadiazole (XIV). A mixture of 6 g of 4-bromo-1,2-naphthalenediamine, m.p. 100–102°, 50 ml of pyridine and 4.2 ml of thionylaniline was heated for 1 hr on the boiling water bath, then cooled, and the solution was treated with 4% hydrochloric acid solution until acid to Congo. The obtained precipitate was filtered and washed with water until neutral. We obtained 6.2 g of substance, which after two recrystallizations from 50% acetic acid (in the presence of carbon) had m.p. 124–125°.

Found %: N 10.56, 10.61; Br 30.42. $C_{10}H_5N_2SBr$. Calculated %: N 10.56; Br 30.19.

X_1',X_2'-Dichloro-1',2'-naphtho-2,1,3-thiadiazole (VI). A solution of 2 g of 1',2'-naphtho-2,1,3-thiadiazole, m.p. 81°, in 50 ml of glacial acetic acid was saturated with chlorine for 15 min at 50° and then concentrated to a sirupy mass. Treatment with 10 ml of hot alcohol gave a precipitate, which was filtered and recrystallized twice from alcohol (in the presence of carbon); the compound was obtained as fine colorless needles with m.p. 138–140°.

Found %: N 11.09, 11.70; S 12.32, 12.51. $C_{10}H_4N_2SCl_2$. Calculated %: N 11.28; S 12.55.

X_1',X_2'-Dibromo-1',2'-naphtho-2,1,3-thiadiazole (VIa). A solution of 2 g of 1',2'-naphtho-2,1,3-thiadiazole, m.p. 81°, in 20 ml of glacial acetic acid was treated with 0.65 ml of bromine in 1.5 ml of glacial acetic acid (heat was evolved), and on cooling we obtained 3.2 g of substance with m.p. 132–132.5° (from alcohol).

Found %: N 8.21, 8.26; Br 46.92, 46.41. $C_{10}H_4N_2SBr_2$. Calculated %: N 8.15; Br 46.51.

Thionylaniline. A mixture of 300 g of aniline hydrochloride, 600 ml of benzene and 125 ml of thionyl chloride was heated under reflux for 12 hr on the water bath, after which the reaction mass was cooled, filtered, and the filtrate was distilled at 12 mm; we obtained 205 g of thionylaniline.

1,2-Naphthalenediamine. Obtained as described in [12] from 18 g of β-naphthylamine hydrochloride and diazotized aniline (from 9.3 g of aniline) in the presence of 18 g of sodium acetate. The obtained azo dye, after reduction with 25 g of zinc dust and 600 ml of 20% acetic acid, was filtered into 150 ml of 20% sulfuric acid. After neutralization with sodium carbonate we obtained 12.5 g of 1,2-naphthalenediamine with m.p. 95–96°.

1',2'-Naphtho-2,1,3-thiadiazole. a) A mixture of 2.3 g of 1,2-naphthalenediamine, m.p. 95–96°, 3 g of thionylaniline and 10 ml of toluene was heated on the water bath for 1 hr, then cooled, and the precipitate was filtered and washed with toluene. The filtrate was evaporated, the residue was treated with 4% hydrochloric acid solution, and the obtained precipitate was filtered and washed with water. The two precipitates were combined and then recrystallized from alcohol to give 2.3 g (90%) of product with m.p. 81° [3].

b) A mixture of 10 g of 1,2-naphthalenediamine sulfate, 15 ml of thionylaniline and 50 ml of pyridine was heated for 1.5 hr on the boiling water bath, after which the cooled mixture was stirred with added 4% hydrochloric acid until acid to Congo. The obtained precipitate was filtered and recrystallized from alcohol; we obtained 6.75 g (75.3%) of product with m.p. 81°.

c) A mixture of 103 g of 1,2-naphthalenediamine (m.p. 95–96°) sulfate, 100 ml of triethylamine and 122 ml of thionylaniline was heated on the boiling water bath for 20 min, then cooled, treated with dilute hydrochloric acid until acid to Congo, and the obtained finely crystalline precipitate was filtered. After recrystallization from alcohol we obtained 89 g (96%) of product with m.p. 81°.

Mixture of 2- and 4-nitro-1-acetamidonaphthalenes. A mixture of 60 g of α-naphthylamine, 55 ml of acetic anhydride and 400 ml of glacial acetic acid was heated on the boiling water bath for 20 min, then cooled, and the solution was treated with nitric acid (d 1.42) in the following manner: 10 ml in one dose at 22° and 19 ml over 15 min at 15°. The clear solution was stirred for 20 hr at 15°, after which the obtained precipitate was filtered to give 68.4 g of substance with m.p. 168–170°. The filtrate was diluted with water and the precipitate (m p 168-174°) (24 g) was recrystallized from alcohol to give 12 g of material with m.p. 188–190°. From the melting point the first compound is 4-nitro-1-acetamidonaphthalene, and the second is the 2-nitro isomer [4].

Mixture of 1-amino-4-nitro- and 1-acetamido-4-nitronaphthalenes. Concentrated sodium hydroxide was added in small portions to 20 g of mixed 2- and 4-nitro-1-acetamidonaphthalenes in 250 ml of hot alcohol until alkaline, after which the reaction mixture was heated for 20 min on the boiling water bath, then allowed to stand for a day, and the obtained 4-nitro-1-naphthylamine was filtered. We obtained 7 g of product with m.p. 191–193° The filtrate was diluted with water and the obtained precipitate was filtered to give 7.64 g of substance (4-nitro--1-acetamidonaphthalene). After recrystallization from alcohol, m.p. 199–201°.

4-Chloro-2-nitro-1-acetamidonaphthalene. A solution of 20 g of 2-nitro-1-acetamidonaphthalene in 60 ml of glacial acetic acid was treated with chlorine for 30 min at 100°. On cooling we obtained 11 g of substance, which after recrystallization from glacial acetic acid melted at 219° [5].

4-Chloro-2-nitro-1-naphthylamine. A mixture of 10 g of 4-chloro-2-nitro-1-acetamidonaphthalene, m.p. 219°, 100 ml of 50% sulfuric acid and 100 ml of alcohol was heated under reflux for 6 hr and then filtered hot. Here we obtained 8.4 g of substance, which after recrystallization from benzene was obtained as orange needles with m.p. 201° [6].

4-Chloro-1,2-naphthalenediamine. Obtained as described in the literature [7] from 3 g of 4-chloro-2-nitro--1-naphthylamine, 180 ml of hot 50% alcohol, 3.5 g of saturated aqueous ammonium chloride solution and zinc dust, the latter added in small portions until the solution decolorized. Filtration of the hot solution on ice in a stream of hydrogen gave 2.6 g of substance with m.p. 92–93°.

1-Acetamidonaphthalene. Obtained as described in [4]: 50 g of 1-naphthylamine was dissolved in 275 ml of 50% acetic acid with heating, then 55 ml of acetic anhydride was added, after which the mixture was cooled and the obtained precipitate was filtered and washed with water; we obtained 56 g of product with m.p. 160°.

4-Bromo-1-acetamidonaphthalene. Obtained as described in the literature by the bromination of 39 g of 1-acetamidonaphthalene, m.p. 160°, in 225 ml of glacial acetic acid with 14 ml of bromine in 37 ml of glacial acetic acid; after filtration and washing with water we obtained 47 g of substance with m.p. 190–192° [9].

4-Bromo-1-acetamido-2-nitronaphthalene. Obtained as described in the literature [10] by the nitration of 21 g of 4-bromo-1-acetamidonaphthalene, m.p. 190–192°, in 300 ml of glacial acetic acid with 6 ml of nitric acid (d 1.5) in 6 ml of glacial acetic acid at 60°. After cooling the mixture and recrystallization of the precipitate from alcohol (using carbon) we obtained 24 g of substance with m.p. 226–230°.

4-Bromo-2-nitro-1-naphthylamine was obtained as described in [11] by the hydrolysis of 20 g of 4-bromo--2-nitro-1-acetamidonaphthalene, m.p. 226–230°, with 50 ml of concd. sulfuric acid at 40–50° for 3 to 4 minutes. The mixture was then poured over ice and the precipitate was recrystallized from alcohol to give 12 g of substance with m.p. 194–196°.

4-Bromo-1,2-naphthalenediamine. Obtained as described in the literature [10] by the reduction of 10 g of 4-bromo-2-nitro-1-naphthylamine in 200 ml of hot 50% alcohol with zinc dust in the presence of 11 g of saturated aqueous ammonium chloride solution, with heating on the water bath (to decolorization of the solution), and subsequent filtration of the hot solution on ice. After the precipitate was filtered in a stream of hydrogen we obtained 5 g of substance with m.p. 100–102°.

SUMMARY

1. The behavior of halogens toward 1',2'-naphtho-2,1,3-thiadiazole was investigated and it was shown that the latter reacts with chlorine and bromine in the same manner as does benzo-2,1,3-thiadiazole, with the respective formation of the dichloro- and dibromodihydro-1',2'-naphtho-2,1,3-thiadiazoles, which when treated with alcoholic KOH solution are converted respectively to the 4'-chloro- and a mixture of the 3'-and 4'-bromo-1',2'-naphtho-2,1,3-thiadiazoles.

2. It was found that 1',2'-naphtho-2,1,3-thiadiazole reacts with chlorine and with bromine in hot acetic acid medium to respectively yield the dichloro- and dibromo-1',2'-naphtho-2,1,3-thiadiazoles with the position of the halogens undetermined.

3. Improvements were made in the synthesis of both the 4-chloro- and 4-bromo-1,2-naphthalenediamines.

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ALKYLATION OF PHENOL BY MOLECULAR COMPOUNDS OF ALCOHOLS WITH BORON FLUORIDE

I. A. Romadan and G. T. Stipniek

Riga Polytechnic Institute
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2193-2196,
July, 1960
Original article submitted July 6, 1959

At the present time a large number of investigations exists on developing methods for the preparation of alkylphenols and alkyl phenyl ethers. These compounds are used in the preparation of antioxidants, oil-soluble synthetic resins, and certain pharmaceuticals. Thus, the products obtained by the condensation of "pentaphen" (p-tert-amylphenol) and p-tert-butylphenol with aldehydes are synthetic resins, soluble in hydrocarbons and drying oils. Usually olefins, alcohols and halo-substituted hydrocarbons are used for the alkylation of phenol. Sulfuric acid, metal halides and boron fluoride are used as the alkylation catalysts.

A large amount of work in this field is being done by S. V. Zavgorodnii and co-workers [1–5]. Using olefins to alkylate phenol, anisole and halo-substituted phenols in the presence of boron fluoride, they obtained a mixture of alkylphenols and alkyl phenyl ethers. It was shown by N. I. Shuikin and L. A. Erivanskaya [6] that anisole, and also the o-, m- and p-methylanisoles are converted on aluminum oxide to alkylated phenols. Phenetole and the n-propyl and isopropyl ethers of phenol behave in a similar manner [7]. I. F. Razvenchuk and S. Z. Kaplan [8, 9] alkylated phenol with isopropyl chloride and isobutyl alcohol on gumbrin that had been treated with gaseous hydrogen chloride. In the first case the yield of alkylphenol fractions was 56%; in the second case the yield of p-tert-butylphenol was 14%; p-tert-butylphenol was also obtained by other authors [10, 11].

Previously we had found that under certain conditions naphthalene, biphenyl, benzene and toluene can be successfully alkylated by molecular compounds of alcohols with boron fluoride. Here the radicals enter mainly in the para-position. For example, the alkylation of biphenyl gave the 4-alkyl- and 4,4'-dialkylbiphenyls [12, 13]; the alkylation of naphthalene with alcohols gave 1,4-dialkylnaphthalenes [14, 15]; the alkylation of benzene and toluene by molecular compounds of alcohols with boron fluoride gave p-dialkylbenzenes [16, 17].

In this paper we investigated the alkylation of phenol with ethyl, propyl, n-butyl, isobutyl and isoamyl alcohols in the presence of boron fluoride under various conditions: at atmospheric and elevated pressures, with solvent and without solvent, and at different temperatures. As a result of the study it was found that both the yields and the proportions of alkylphenols to alkyl phenyl ethers depend on the temperature and the solvent. Nearly pure p-alkylphenols are obtained in up to 70–80% yield, based on phenol, when phenol is alkylated by molecular compounds of alcohols with boron fluoride (strongly acidic substances). A mixture of alkylphenols and alkyl phenyl ethers in the ratio 80–85: 20–25 is obtained when the alkylation reactions are run under pressure. The alkyl phenyl ethers are easily isomerized to the p-alkylphenols even on distillation. The ethers are isomerized with even greater ease if their solution in carbon tetrachloride is heated for a short time at 130–140° and 12–15 atm. The experimental data obtained by us are given in Table 1 and plotted in the Figure.

During our study it was found that a part of the phenol is converted to tar when heated in an autoclave at 160–170°. In order to establish the optimum temperature at which both the decomposition of the molecular compound of alcohol with boron fluoride and the alkylation proceed simultaneously, we measured the temperature in the reaction system (using a thermocouple and potentiometer) at 5 minute intervals. It was found that each alcohol has its own maximum temperature at which intense decomposition begins, accompanied by the evolution of heat.

TABLE 1. Alkylation of Phenol by Molecular Compounds of Alcohols With Boron Fluoride

Name of alcohol	Solvent	Reaction temperature	Reaction time (in minutes)	Pressure (in atm)	Yield (in %)		Principal product	Boiling point	Melting point
					Alkylphenols	Ethers			
Ethyl	CCl_4	155°	180	20	–	18	Phenetole	167°	–
n-Propyl	–	167	180	18	21	–	p-Isopropylphenol	228	–
n-Propyl	CCl_4	142	160	20	70	20	p-Isopropylphenol	224	61°
Isopropyl	–	137	200	15	45	16	p-Isopropylphenol	224	61
Isopropyl	CCl_4	134	180	22	68	15	p-Isopropylphenol	224	61
n-Butyl	CCl_4	172	200	20	43	17	p-sec-butylphenol	230–232	–
n-Butyl	CCl_4	128	180	15	76	16	p-sec-butylphenol	–	–
Isobutyl	–	170	60	1	32	14	p-Tert-butylphenol	228	98–99
Isobutyl	–	170	120	1	47	16	p-Tert-butylphenol	–	–
Isobutyl	$C_6H_5NO_2$	165	120	1	23	–	Tar	–	–
Isobutyl	CCl_4	165	120	25	56	20	p-Tert-butylphenol	227–228	98–99
Isobutyl	CCl_4	120	30	15	71	15	p-Tert-butylphenol	–	–
Isoamyl	–	164	60	12	53	18	p-Tert-amylphenol	245–247	93
Isoamyl	CCl_4	135	60	16	78	19	p-Tert-amylphenol	–	–
Isoamyl	$C_6H_5NO_2$	135	60	14	34	–	p-Tert-amylphenol	–	–

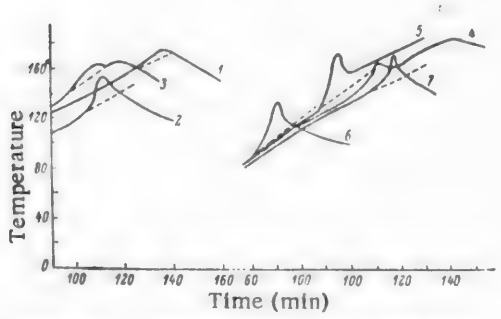
TABLE 2. Properties of Obtained Compounds

Name of compound and reference	Boiling point	Melting point	Molecular weight		Found (%)		Calculated (%)	
			found	calculated	C	H	C	H
p-Isopropylphenol [18]	215–217°	–	138	136.1	79.31	8.75	79.35	8.89
p-Sec-butylphenol [18]	239–240	58–59°	149	150.2	80.01	9.40	79.95	9.39
p-Tert-butylphenol [19]	235–236	99	147	150.2	79.81	9.44	79.95	9.39
p-Tert-amylphenol [20]	264–266	93	165	164.2	80.39	9.83	80.44	9.83
p-Tert-butylphenyl butyl ether	264	–	208	206	81.86	10.81	81.95	10.75
Isobutyl phenyl ether [21]	197–199	–	–	–	80.01	9.27	79.95	9.39
p-Sec-butylphenyl butyl ether	257–258	–	204	206	81.86	10.67	81.95	10.75
p-Tert-amylphenyl amyl ether	278–280	–	230	234	81.91	11.06	81.99	11.18
Isoamyl phenyl ether [22]	218–220	–	–	–	80.49	9.31	80.44	9.38

The process of decomposition and alkylation takes place in a very short period of time, which can be seen from the curves given for the different alcohols. Somewhat unexpected is the process for the decomposition of the propyl alcohols, especially isopropyl alcohol, for which a peak in the range 60–70° is characteristic. All of the other alcohols give jumps in the range 110–135°. All of the subsequent condensations were carried out on the basis of the obtained data.

EXPERIMENTAL

The molecular compounds were prepared by saturating the dried and distilled alcohols with boron fluoride under ice cooling. The obtained molecular compounds, corresponding to the formula $2ROH \cdot BF_3$, were used for alkylation without prior distillation. A three-necked flask, fitted with a reflux condenser and mechanical stirrer, was used when the alkylation was run at atmospheric pressure, and the reaction mass was heated in an oil bath. The molecular compounds were added in small portions from a dropping funnel to a boiling solution of phenol in carbon tetrachloride. The entire process of adding the alcohol and subsequent heating was terminated after 6–8 hours. A 1-liter, electrically heated, rotated autoclave was used when the reaction was run under pressure. The temperature was raised gradually to the optimum, which required 1–1.5 hr. The heating was stopped just as soon as the molecular compound began to decompose with intensity (from the potentiometer and manometer readings), but the mixing was maintained until the temperature had dropped to 60–70°. After cooling, the reaction mass was poured out of the autoclave, where, as a rule, a green crystalline mass remained on the bottom. The oily product was separated from the highly acid bottom layer, followed by washing with sodium carbonate solution until neutral. Then the alkylate was treated with 1.5 volumes of 10% NaOH solution and allowed to stand for 10–12 hours. The liquid separated into two layers: the upper layer represented the phenolates of the alkylation products, while the lower layer was a solution of the ethers in carbon tetrachloride. If the reaction was run without solvent, then to separate the phenols from the nonphenols the mixture was diluted with either benzene or carbon tetrachloride, and the phenolates were decomposed by bubbling in carbon dioxide. The phenols and nonphenols were distilled separately, first from a flask fitted with a Vigreux column, and then through a vacuum column with an efficiency of 50 theoretical plates.



Alkylation of phenol by molecular compounds of boron fluoride with various alcohols. 1) $C_2H_5OH \cdot BF_3 + C_6H_5OH$; 2) 2 iso-$C_4H_9OH \times BF_3 + C_6H_5OH$; 3) 2 iso-$C_5H_{11}OH \cdot BF_3 + C_6H_5OH$; 4) 2 n-$C_3H_7OH \cdot BF_3 + C_6H_5OH$; 5) 2 n-$C_3H_7OH \times BF_3$; 6) 2 iso-$C_3H_7OH \cdot BF_3 + C_6H_5OH$; 7) 2 n-$C_4H_9OH \cdot BF_3 + C_6H_5OH$.

As can be seen from the data in Table 1, the best results were obtained when the alkylation was run under pressure in carbon tetrachloride solution. In nitrobenzene the reaction goes with smaller yields, with the formation of tars; here the nitrobenzene is partially alkylated. Nearly pure p-alkylphenols are formed under the indicated conditions, whereas the ortho-isomers are formed in very small amounts (2–3%). Dialkylphenols are not formed when a solvent is used, whereas in its absence they are obtained in a yield of 15–20% on the total amount of alkylphenols formed. The properties of the obtained compounds are listed in Table 2.

SUMMARY

1. The alkylation of phenol by molecular compounds of alcohols with boron fluoride gave mainly p-alkylphenols, the yields of which reach 76–80%.

2. The alkylation of phenol with isobutyl and isoamyl alcohols gave p-alkylphenols with tertiary radicals. p-Isopropylphenol was obtained when the alkylation with n-propyl and isopropyl alcohols was run under pressure.

3. The alkyl phenyl ethers are completely isomerized to p-alkylphenols when their solution in carbon tetrachloride is heated at 140–150° under a pressure of 12–15 atm.

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ARALKYLATION OF PHENOL BY STYRENE AND α-METHYLSTYRENE

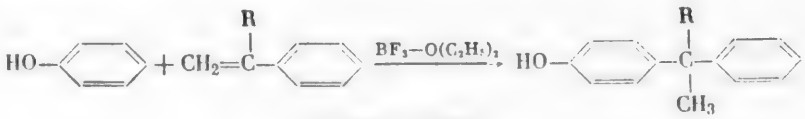
S. V. Zavgorodnii, B. A. Zaitsev, and D. P. El'chinov

Voronezh State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2196-2199, July, 1960
Original article submitted July 6, 1959

Alkylation of phenols by olefins in presence of various catalysts including boron fluoride [1] has been studied fairly extensively. On the other hand the aralkylation of phenols by arylolefins has not been adequately studied in spite of the definite practical importance of the products of this reaction.

We have studied the reaction of phenol with styrene and α-methylstyrene in presence of catalysts—boron fluoride etherate and boron fluoride + 75% orthophosphoric acid. Styrene and α-methylstyrene are found to react with phenol in presence of these catalysts to form aralkylphenols. Styrene gives a mixture of mono- and diarylalkylphenols with a total yield, depending on the conditions, of 32-30%; α-methylstyrene gives p-hydroxydiphenyldimethylmethane in a yield of up to 60% together with a small quantity of resinous products from which specific compounds could not be isolated. Aralkylation in both cases is accompanied by polymerization of the arylolefins. This occurs with especial facility in the case of styrene, so that under certain conditions polymerization is the main reaction. For example, reaction of phenol with styrene in presence of boron fluoride etherate in molar ratios of 1 : 1 : 0.04 at room temperature for 24 days gives hydroxydiphenylmethymethane in a yield of 18%, together with polystyrene in a yield of 61% (calculated on the styrene). With the same molar ratios but in presence of boron fluoride + 75% orthophosphoric acid at 18-22° for 12 days the yields of hydroxydiphenylmethylmethanes are 4%. α-Methylstyrene is less susceptible to polymerization; apart from giving resinous polymers, it partly dimerizes to the crystalline 1,1,3-trimethyl-3-phenylindane which distils with the p-hydroxydiphenyldimethylmethane. The most favorable conditions for production of hydroxydiphenylmethylmethane (yield 46%) are a phenol, styrene, boron fluoride etherate molar ratio of 2 : 1 : 0.06, a temperature of 95-97° and a reaction period of 2 hr. p-Hydroxydiphenyldimethylmethane is obtained in the best yield (60%) by reaction of phenol with α-methylstyrene in presence of boron fluoride etherate (molar ratio of 3 : 1 : 0.15) at 80-83° for 9 hr. The reaction can be represented by the following general equation:



(R = H or CH_3).

EXPERIMENTAL

Freshly distilled commercial styrene was used (b.p. 53° at 18 mm, d_4^{20} 0.9030). α-Methylstyrene was isolated from the methylstyrene fraction of secondary products of phenol—acetone production by numerous vacuum distillations. It was thereby obtained in 99% purity (b.p. 40-45° at 5 mm, d_4^{20} 0.9018, n_D^{20} 1.5330).

Reaction of phenol with styrene. Into a 100 ml flask were charged 10.4 g of styrene and the appropriate weight of phenol. The mixture was cooled to -5° and the calculated amount of boron fluoride etherate added with vigorous shaking. The flask was then closed, and stood for 1-2 hr in a freezing mixture or for a given time at room tempera-

ture or heated on a boiling water bath. The reaction products were treated with 5% sodium hydroxide solution, the insoluble styrene polymers were separated, and the phenolic compounds recovered from the alkaline solution by treatment with 5-10% hydrochloric acid. The phenols were then dried and distilled. Unreacted phenol first came over, followed by reaction products in the form of two fractions. A considerable quantity of resin remained in the flask and broke down when heated above 200-280° (7-15 mm). Typical experiments are detailed in Table 1.

TABLE 1. Aralkylation of Phenol by Styrene

Phenol, styrene, boron fluoride etherate molar ratio	Reaction temperature	Duration (hr)	Obtained		
			Hydroxydiphenylmethylmethane fraction (%)	Products boiling above 200° at 12-16 mm (in g)	Resins (in g)
1:1:0.04	18–22	24 days	17.7	3.3	4.0
1:1:0.04	95–97	2	22.2	1.9	4.1
1:1:0.04	95–97	8	29.8	3.9	4.8
2:1:0.06	18–22	24	35.3	2.1	2.9
2:1:0.06	95–97	2	46.0	4.4	2.6
2:1:0.06	95–97	8	32.8	4.2	4.6

In the presence of boron fluoride + 75% orthophosphoric acid the main reaction was polymerization of styrene. Results are therefore omitted.

p-Hydroxydiphenylmethylmethane consisted of a colorless liquid after two distillations of the hydroxydiphenylmethane fraction.

B.p. 162-165° (7–8 mm), d_4^{20} 1.0870, n_D^{20} 1.5942, MR_D 61.86; Calc. 61.17.
Found %: C 84.78, 84.49; H 7.32, 7.19. M 202.0. $C_{14}H_{14}O$. Calculated %: C 84.80; H 7.12. M 198.0.

p-Hydroxydiphenylmethylmethane benzoate: obtained by mixing hydroxydiphenylmethylmethane, dissolved in 20% sodium hydroxide, with benzoyl chloride; colorless crystals with m.p. 79-81°. The literature [2] gives m.p. 83°.

Found %: C 83.10, 83.01; H 6.14, 6.26. $C_{21}H_{18}O_2$. Calculated %: C 83.41; H 6.00.

From the products boiling above 200° (12-16 mm) was isolated a compound which was assumed to be di(α-phenylethyl) phenol with b.p. 234-240° (10 mm), d_4^{20} 1.0830, n_D^{20} 1.6000, MR 95.48; calcd. 94.52.

Found: M 294.8. $C_{22}H_{22}O$. Calculated: M 302.3

Reaction of phenol with α-methylstyrene. In a three-necked flask, fitted with stirrer, thermometer and dropping funnel, were mixed 29.5 g of α-methylstyrene and the calculated quantity of phenol. The mixture was stirred and at the predetermined temperature boron fluoride etherate was added dropwise. After the reaction, the mixture was treated with two portions of water (100 ml each), dried with sodium sulfate and distilled. Unreacted phenol and α-methylstyrene came over up to 72° (15 mm), and these were followed by p-hydroxydiphenyldimethylmethane together with a little 1,1,3-trimethyl-3-phenylindane. Typical experiments are set forth in Table 2.

p-Hydroxydiphenyldimethylmethane: in the freshly distilled form a colorless liquid with b.p. 152-153° (4 mm); readily crystallizes on standing to give white needles with m.p. 72° (from ligroine). The structure was verified by conversion into the previously known p-(α,α-dimethylbenzyl) phenoxyacetic acid with m.p. 115° (from hot water). It was purified from α-methylstyrene dimer via the alkali-soluble sodium salt or by recrystallization from ligroine.

1,1,3-Trimethyl-3-phenylindane: stout, colorless crystals (when slowly crystallized) with m.p. 51-52° (from alcohol). A mixture with the dimer obtained from α-methylstyrene in presence of sulfuric acid did not show a depressed melting point. It was isolated from the mother liquor, after recrystallization of p-hydroxydiphenyldimethylmethane, as indicated above.

SUMMARY

The aralkylation of phenol by styrene and α-methylstyrene was studied in presence of boron fluoride etherate, and a polymerizing effect of the catalyst was observed, especially in the case of styrene.

p-Hydroxydiphenyldimethylmethane (from the phenol–α-methylstyrene–boron fluoride etherate molar ratio 1:1:0.07) and the dimer of α-methylstyrene – 1,1,3-trimethyl-3-phenylindane were isolated.

TABLE 2. Aralkylation of Phenol by α-Methylstyrene

Phenol, α-methyl styrene, boron fluoride etherate molar ratio	Reaction temperature	Duration (hr)	Obtained		
			p-Hydroxydi-phenyldimethyl-methane (%)	1,1,3-Trimethyl--3-phenylindane (in % of the methylstyrene)	Resins (in g)
1:1:0.03	58–60	6	3.9	–	10.0
1:1:0.07	18–20	24	32.2	–	7.0
1:1:0.07	58–60	3	33.9	–	10.4
1:1:0.07	58–60	6	36.0	–	7.0
2:1:0.07	58–60	6	44.5	–	6.2
3:1:0.07	58–60	6	53.6	1.8	3.0
3:1:0.15	80–84	6	57.0	2.4	5.6
3:1:0.15	80–82	6	59.5	2.4	6.9
4:1:0.15	80–83	6	56.1	3.2	5.1

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INVESTIGATIONS ON FURANS

VI. *β-CHLOROETHYLAMINES OF THE FURAN SERIES

K. Yu. Novitskii, Yu. K. Yur'ev, Yu. A. Afanas'eva, I. G. Bolesov, and A. F. Oleinik

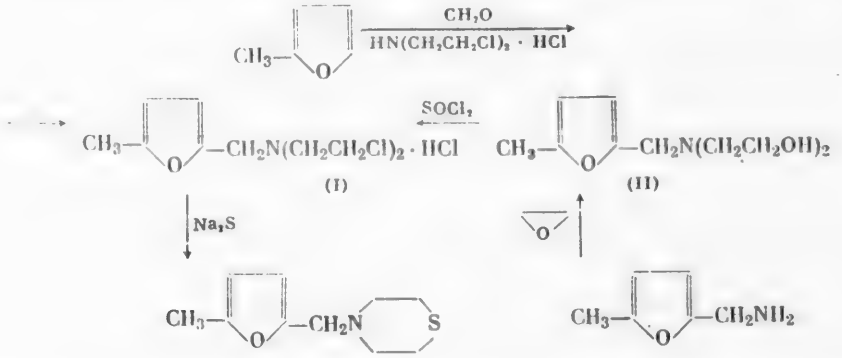
Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2199-2202, July, 1959
Original article submitted July 3, 1959

In the present work we investigated the possibility of aminomethylation of 2-methylfuran by the Mannich reaction with the help of β,β'-dichlorodiethylamine.

We know from the work of Holdren and Hixon [1] that formaldehyde and amine hydrochlorides aminomethylate the furan ring in the 5 position but the yields of products vary considerably. Gill and Ing [2] recently used dimethylamine hydrochloride and attained high yields of products of aminomethylation of 2-methylfuran, furfuryl alcohol and dimethylfurfurylamine.

We established that the aminomethylation of 2-methylfuran by β,β'-dichlorodiethylamine proceeds with facility and leads to a high yield of the hydrochloride of di(β-chloroethyl)-2-(5-methylfurfuryl)amine (I). We also obtained the same compound by another route: action of ethylene oxide on 5-methyl-2-furfurylamine [formed on reduction of the oxime of 5-methylfurfural together with di-(5-methylfurfuryl-2)-amine] led to di(β-hydroxyethyl)-2-(5-methylfurfuryl) amine (II), which on treatment with thionyl chloride gave the dichloride (I).



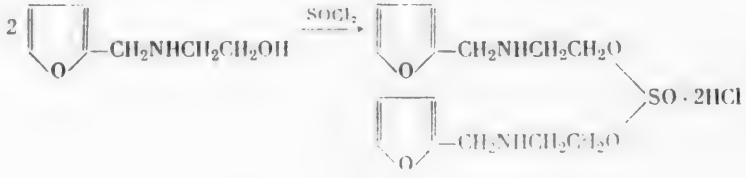
The structure of dichloride (I) was also confirmed by its conversion to N-(5-methylfurfuryl-2-)-thiomorpholine with the help of sodium sulfide.

In one of the previous papers [3] we reported that treatment of di-(β-hydroxyethyl)-2-furfurylamine with thionyl chloride and then with sodium sulfide gave N-(2-furfuryl) thiomorpholine without previous isolation of the di-(β-chloroethyl)-2-furfurylamine. In the present work we showed that the latter compound is also obtained by this route in a yield of 90%.

*Communication IV: Doklady Akad. Nauk SSSR 126, 806 (1959).

Continuing our study of the action of thionyl chloride on other hydroxyalkylaminomethylfurans, we found that N-(β-hydroxyethyl) difurfurylamine is easily converted into the hydrochloride of N-(β-chloroethyl) difurfurylamine (the furan analog of the adrenaline antagonistic—dibenzamine [4]).

We treated N-(β-hydroxyethyl) furfurylamine with thionyl chloride and obtained the dihydrochloride of di-[β-(2-furfurylamino)ethyl] sulfite:



EXPERIMENTAL

Hydrochloride of di-(β-chloroethyl)-2-furfurylamine (I). To 18.5 g (0.1 mole) of di-(β-hydroxyethyl)-2-furfurylamine [1] in 50 ml of anhydrous chloroform, in a flask fitted with dropping funnel and reflux condenser capped by a calcium chloride tube, was added 15.9 ml (0.22 mole) of freshly distilled thionyl chloride in 20 ml of chloroform dropwise in the course of an hour. The mixture was then heated for 1.5 hr on a water bath at 50° and stood overnight. After the solvent had been taken off in vacuo at 30°, addition was made of 50 ml of chloroform; this was then distilled off and 50 ml of benzene was run in. When the benzene was distilled off in vacuo, the residue crystallized completely. The crystals were washed with cold benzene. Yield 23.2 g (90%); m.p. 87-87.5° (from absolute alcohol).

Found %: C 42.17, 41.94; H 5.46, 5.46; N 5.45, 5.38; Cl 41.18, 41.10. $C_9H_{14}ONCl_3$. Calculated %: C 41.80; H 5.46; N 5.42; Cl 41.13.

Hydrochloride of N-(β-chloroethyl)difurfurylamine. Prepared as described above from 36 g of (0.16 mole) of N-(β-hydroxyethyl) difurfurylamine [1] in 50 ml of chloroform and 14 ml (0.19 mole) of thionyl chloride in 20 ml of chloroform. Yield 32 g (84%); m.p. 116-117° (from chloroform).

Found %: N 4.96, 5.09; Cl 25.87, 25.93. $C_{12}H_{15}O_2NCl_2$. Calculated %: N 5.07; Cl 25.68.

Dihydrochloride of di-[β-(2-furfurylamino)ethyl] sulfite. Prepared by addition in 15 min of a solution of thionyl chloride in 10 ml of chloroform to an ice-cooled solution of 7.5 g (0.05 mole) of β-hydroxyethylfurfurylamine in 20 ml of chloroform. Yield 8 g (80%); m.p. 126-126.5° (from absolute alcohol).

Found %: C 41.97, 41.87; H 5.72, 5.67; Cl 17.83, 17.69. $C_{14}H_{22}O_5N_2Cl_2S$. Calculated %: C 41.90; H 5.53; Cl 17.67.

Hydrochloride of di-(β-chloroethyl)-2-(5-methylfurfuryl)amine (I) (method A). Dropwise addition of 15 g (0.18 mole) of 2-methylfuran was made to a mixture of 25 g (0.14 mole) of di-(β-chloroethylamine) hydrochloride [5] and 14 ml of 30% formaldehyde at 15° in a four-necked flask equipped with stirrer, reflux condenser, dropping funnel and thermometer. The mixture was stirred for an hour. After distillation of the water and excess of 2-methylfuran in vacuo, the residue crystallized completely. Yield 34 g (93%); m.p. 121-122° (from alcohol and then from chloroform-ether).

Found %: N 5.26, 5.43; Cl 38.83, 38.91. $C_{10}H_{16}ONCl_3$. Calculated %: N 5.14; Cl 39.02.

N-(5-Methylfurfuryl-2)thiomorpholine-1,4. A mixture of 27.2 g (0.1 mole) of hydrochloride (I) and 96 g (0.4 mole) of crystalline sodium sulfide in 150 ml of alcohol was refluxed for 5 hr. The alcoholic solution was separated and the alcohol distilled off in vacuo; the residue was thrice extracted with ligroine. Distillation of the solvent followed by distillation of the residue in vacuo gave 7.6 g (38%).

B.p. 115-116°, (2mm), n_D^{20} 1.5402, d_4^{20} 1.1080, MR_D 55.80. $C_{10}H_{15}ONS_{F2}$. Calculated 56.70.

Found %: C 60.97, 61.20; H 7.60, 7.61; S 16.28, 16.31. $C_{10}H_{15}ONS$. Calculated %: C60.88; H 7.81; S 16.25.

Picrate: m.p. 162° (from alcohol).

Found %: C 45.26, 45.46; H 4.42, 4.42; S 7.26, 7.55. $C_{16}H_{18}O_8N_4S$. Calculated %: C 45.07; H 4.25; S 7.52.

5-Methylfurfurylamine. From 87 g (0.8 mole) of 5-methylfurfural, 64 g (0.93 mole) of hydroxylamine hydrochloride and 124 g (0.9 mole) of sodium acetate was obtained 80 g of the oxime of 5-methylfurfural; m.p. 114°. Literature [6, 7]: m.p. 112-113°, 110-112°.

Reduction of the oxime of 5-methylfurfural (50 g or 0.4 mole) was effected with zinc dust (143 g) and acetic acid (285 ml). The following products were obtained: a) 16 g (40%) of 5-methylfurfurylamine:

B.p. 55° (7 mm), n_D^{20} 1.4830, d_4^{20} 0.9986, MR_D 31.78. $C_6H_9ON_{F2}$. Calculated 31.84.

Found %: C 64.85, 64.60; H 8.44, 8.45. C_6H_9ON. Calculated %: C 64.84; H 8.16.

b) Di-(5-methylfurfuryl)amine; yield 2 g.

B.p. 112° (2 mm), n_D^{20} 1.5136, d_4^{20} 1.0631, MR_D 58.09. $C_{12}H_{15}ON_{F4}$. Calculated 58.23.

Found %: N 7.06, 7.10. $C_{12}H_{15}O_2N$. Calculated %: N 6.82.

Di-(β-hydroxyethyl)-2-(5-methylfurfuryl)amine (II). A uniform stream of ethylene oxide (11.9 g or 0.27 mole) was passed through a gas-leading tube into a large test tube (also fitted with a reflux condenser) containing 15 g (0.135 mole) of 5-methylfurfurylamine, 2 ml of alcohol, and a few drops of water. Vacuum distillation of the reaction products gave: a) 1.8 g of unchanged amine; b) 4.8 g (26% calculated on the reacted amine) of N-(β-hydroxyethyl)-5-methylfurfurylamine:

B.p. 138° (9 mm), n_D^{20} 1.4965, d_4^{20} 1.0890; literature data [2]: b.p. 120° (8 mm), n_D^{20} 1.4955, d_4^{20} 1.0893.

c) 11.7 g (49% calculated on the reacted amine) of di-(β-hydroxyethyl)-2-(5-methylfurfuryl)amine:

B.p. 144° (2 mm), n_D^{20} 1.5063, d_4^{20} 1.1143, MR_D 53.16. $C_{10}H_{17}O_3N_{F2}$. Calculated 53.88.

Found %: C 60.48, 60.56; H 8.49, 8.49. $C_{10}H_{17}O_3N$. Calculated %: C 60.30; H 8.60.

Picrate: m.p. 128° (from alcohol).

Found %: N 13.32, 13.49. $C_{16}H_{20}O_{10}N_4$. Calculated %: N 13.08.

Di-(β-chloroethyl)-2-(5-methylfurfuryl)amine hydrochloride (I) (method B). Dropwise addition of 5.2 g (0.07 mole) of thionyl chloride in 10 ml of chloroform was made in the course of 40 min to a solution of 6 g (0.03 mole) of (II) in 25 ml of anhydrous chloroform in a flask fitted with dropping funnel and reflux condenser. The mixture was heated for 1.5 hr at 45-50° and thereafter for another 15 min after addition of active carbon. The mass was filtered, the chloroform and excess thionyl chloride were distilled off in vacuo, and 50 ml of anhydrous chloroform was added to the residue. The chloroform was then distilled off in vacuo, and 50 ml of anhydrous benzene was added. The latter, too, was then distilled off in vacuo. The residue crystallized completely. Yield 6.7 g (82%); m.p. 119°. Recrystallization from benzene raised the m.p. to 121°. No depression of m.p. in admixture with the product obtained by method A.

SUMMARY

The hydrochloride of di-(β-chloroethyl)-2-(5-methylfurfuryl)amine can be obtained in good yield by the action of ethylene oxide and thionyl chloride on 5-methylfurfurylamine, as well as by aminomethylation of 2-methylfuran by formaldehyde and β,β'-dichlorodiethylamine hydrochloride. The hydrochlorides of di-(β-chloroethyl)furfurylamine and β-(chloroethyl)difurfurylamine were prepared, also in high yield, by the action of thionyl chloride on the corresponding diols.

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*Original Russian pagination. See C. B. translation.

INVESTIGATIONS ON FURANS

VII. 2,5-BIS(CHLOROMETHYL)FURAN IN THE SYNTHESIS OF 2,5-BIS(ALKOXYMETHYL)- AND 2,5-BIS(ALKYLMERCAPTOMETHYL)FURANS

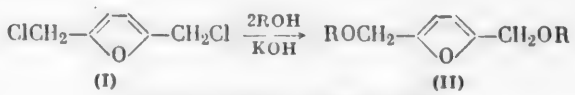
K. Yu. Novitskii, V. P. Volkov, P. V. Kostetskii, and Yu. K. Yur'ev

Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2203-2207, July, 1960
Original article submitted July 15, 1959

In one of the previous papers in this series [1] it was shown that interaction of 2,5-bis(chloromethyl)furan (I) with secondary amines leads to formation of 2,5-bis(dialkylamino)furans in high yield. In the present work we studied the reactions of 2,5-bis(chloromethyl)furan with alcohols and mercaptans and obtained previously undescribed 2,5-bis(alkoxymethyl)- and 2,5-bis(alkylmercaptomethyl)furans.

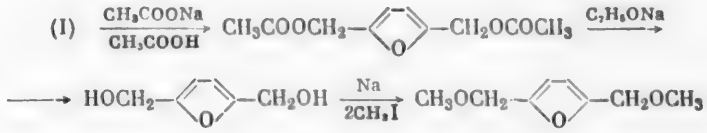
Replacement of the two chlorine atoms of (I) alkoxy groups takes place with facility by the action of alcohols in presence of caustic alkali; the yield of the corresponding ethers—2,5-bis(alkoxymethyl)furans—60-70%.



(I) (II)

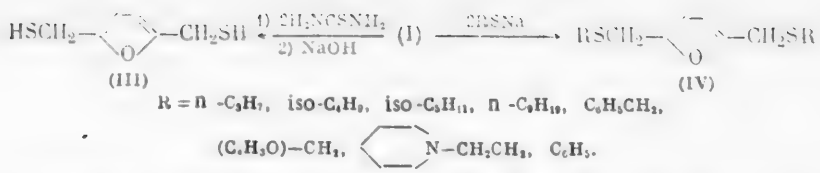
R = CH_3, C_2H_5, n-C_4H_9, n-C_5H_{11}.

The yield of ethers is raised to 74-82% if sodium alkoxides are used in place of the corresponding alcohols. We also prepared 2,5-bis(methoxymethyl)furan by methylation of 2,5-bis(hydroxymethyl)furan which was obtained by alcoholysis of 2,5-bis(acetoxymethyl)furan. The latter was synthesized by reaction of 2,5-bis(chloromethyl)furan with sodium acetate.



Reaction of 2,5-bis(chloromethyl)furan with thiourea and subsequent decomposition of the resulting bis-isothiuronium salt gave 2,5-bis(mercaptomethyl)furan. The latter was also identified in the form of the bis-phenylthiourethane.

The great mobility of the chlorine in 2,5-bis(chloromethyl)furan becomes particularly manifest when it reacts with sodium mercaptides. The corresponding 2,5-bis(alkymercaptomethyl)furans (IV) are formed in a yield of 72-89%; the yield of 2,5-bis(phenylmercaptomethyl)furan is 60%.



(III) (IV)

R = n -C_3H_7, iso-C_4H_9, iso-C_5H_{11}, n -C_9H_{19}, $C_6H_5CH_2$,

(C_4H_3O)—CH_2, , C_6H_5.

The first two representatives of the bis-sulfides (R=C_3H_7, iso-C_4H_9) give crystalline complexes with mercuric chloride; the others form oils. The mercuric chloride complexes do not melt sharply and at above 120° (in a sealed capillary) they blacken and decompose. 2,5-Bis(benzylmercaptomethyl)furan and 2,5-bis(furfurylmercaptomethyl)-furan were also prepared by interaction of the bis-sodium derivative of 2,5-bis(mercaptomethyl)furan (III) with benzyl chloride and furfuryl chloride respectively.

EXPERIMENTAL

1. Synthesis of 2,5-Bis(alkoxymethyl)furans (II)

A. A three-necked, round-bottomed flask, fitted with reflux condenser, dropping funnel and stirrer, was charged with 100 ml of anhydrous alkanol and 4.5 g (0.08 mole) of finely pulverized potassium hydroxide; dropwise addition was made in the course of 15 min, with vigorous stirring, of a solution of 3.3 g (0.02 mole) of 2,5-bis(chloromethyl)furan in 10 ml of the same alkanol; the mass was stirred for 4-5 hr at 20° and for 2 hr at 60-70°. The mixture was cooled, the precipitate filtered off, the alkanol distilled off in vacuo, and the liquid residue twice washed with water. The aqueous solution was repeatedly extracted with ether; the ethereal extracts were combined with the organic layer and dried with magnesium sulfate. After the ether had been taken off, the residue was distilled in vacuo over sodium.

B. Into a three-necked flask, containing a solution of 1.84 g (0.08 g-atom) of sodium in 100 ml of anhydrous alkanol, was introduced dropwise a solution of 3.3 g (0.02 mole) of 2,5-bis(chloromethyl)furan in 10 ml of the same alkanol with vigorous stirring and cooling. Stirring was then continued for 30 min at 20° and for 5-6 hr on a boiling water bath. Reaction products were isolated as described in A.

Constants and yields of the prepared 2,5-bis(alkoxymethyl)furans are set forth in the table.

Constants and Yields of 2,5-Bis(alkoxymethyl)furans

Structure of (II) where R =	Yield		Boiling point (pressure in mm)	n^{20}_D	d^{20}_4	MR_D		Found (%)		Calculated (%)	
	method A	method B				found	calculated	C	H	C	H
CH_3	61	74	46—47 (4)	1.4660	1.0639	40.70	40.95	61.42, 61.60	8.14, 8.21	61.52	7.74
C_2H_5	70	82	80—81 (4)	1.4622	1.0141	50.00	50.18	65.14, 65.32	8.94, 9.03	65.20	8.76
n -C_4H_9	65	80	110—111 (2)	1.4610	0.9638	68.44	68.65	69.63, 69.66	9.97, 9.99	69.94	10.06
n-C_5H_{11}	70	78	133—134 (2)	1.4602	0.9466	77.56	77.88	70.89, 71.03	10.64, 10.71	71.59	10.52

2,5-Bis(acetoxymethyl)furan. A three-necked, round-bottomed flask, fitted with a reflux condenser and stirrer, was charged with 100 ml of glacial acetic acid, 6.6 g (0.04 mole) of 2,5-bis(chloromethyl)furan and 7.2 g (0.088 mole) of finely pulverized anhydrous sodium acetate. The mixture was stirred for 5 hr at 60-70° and stood for 24 hr at 20°. The precipitate was filtered and the acetic acid distilled off in vacuo. The solid residue was treated with boiling carbon tetrachloride, filtered and cooled. The crystals were suction-filtered and dried. Yield 6.1 g (72%); m.p. 63-64° (from ligroine).

Literature data [2]: m.p. 64°.

2,5-Bis(hydroxymethyl)furan. To a solution of 0.1 g (0.004 g-atom) of sodium in 50 ml of anhydrous alcohol was added 4.24 g (0.02 mole) of 2,5-bis(acetoxymethyl)furan. The mixture was vigorously stirred for 30 min and stood at 20° for three days. The alcohol was distilled off in vacuo, and the solid residue treated with boiling benzene, filtered and cooled. The crystals were suction-filtered and dried. Yield 2.2 g (85%); m.p. 79-80° (from benzene).

Found %: C 56.14, 56.31; H 6.37, 6.39. $C_6H_8O_3$. Calculated %: C 56.25; H 6.30.

Literature data: m.p. 75.5-77° [3]; m.p. 80° [2].

2,5-Bis(methoxymethyl)furan. To a suspension of the bis-sodium derivative of 2,5-bis(hydroxymethyl)furan [from 0.64 g (0.005 mole) of 2,5-bis(hydroxymethyl)furan and 0.23 g (0.01 g-atom) of sodium in 100 ml of anhydrous benzene] was added dropwise (in 15 min) 2.84 g (0.02 mole) of methyl iodide in 10 ml of anhydrous benzene. The mixture was stirred at 20° for 4 hr and on a boiling water bath for 1 hr. The precipitate was filtered, and the benzene solution was washed with water and dried with magnesium sulfate. The benzene was distilled in vacuo and the residue distilled over sodium. Yield 0.50 g (64%).

B.p. 48-49° (5 mm), n_D^{20} 1.4658, d_4^{20} 1.0624, MR_D 40.72. $C_8H_{12}O_3F_2$. Calculated 40.95

2. Synthesis of 2,5-Bis(mercaptomethyl)furan

A solution of 5.0 g (0.03 mole) of 2,5-bis(chloromethyl)furan and 4.5 g (0.06 mole) of thiourea in 200 ml of anhydrous acetone was boiled on a water bath for 4 hr. The acetone was then distilled off and to the residual bis-isothiuronium salt was added a solution of 4.0 g (0.09 mole) of sodium hydroxide in 50 ml of water and 20 ml of benzene. The mixture was heated on a boiling water bath for 2-3 hr and cooled to 0-5°; dropwise addition was then made of 10 ml of glacial acetic acid. The benzene layer was separated and the aqueous layer thrice extracted with benzene. The benzene extracts were washed with sodium bicarbonate and then with water and dried with magnesium sulfate. Removal of the benzene in vacuo and distillation of the residue were effected in a nitrogen stream. Yield 1.5 g (31%).

B.p. 100-102° (5 mm), n_D^{20} 1.5738, d_4^{20} 1.1946, MR_D 44.24. $C_6H_8OS_2F_2$. Calculated 43.80.

Bis-phenylthiourethane: m.p. 167-168° (from toluene).

Found %: C 59.99, 60.15; H 4.48, 4.54. $C_{20}H_{18}O_3N_2S_2$. Calculated %: C 60.27; H 4.55.

3. Synthesis of 2,5-Bis(alkylmercaptomethyl)furans (V)

a) 2,5-Bis(n-propylmercaptomethyl)furan. In the course of 25 min 7.6 g (0.01 mole) of n-propylmercaptan was stirred dropwise into a finely dispersed suspension of 1.84 g (0.08 g-atom) of sodium in 50 ml of anhydrous toluene at 45-50°; stirring was continued for 4 hr at 20°. A solution of 6.6 g (0.04 mole) of 2,5-bis(chloromethyl)-furan in 10 ml of toluene was then added dropwise, and the mixture heated for 2-3 hr on a boiling water bath. Cooling was followed by addition of 20 ml of water, the toluene layer was separated and the aqueous layer extracted with ether. The organic layer was dried with magnesium sulfate and the solvents distilled off in vacuo. Distillation of the residue gave 8.1 g (83%).

B.p. 133-134° (1 mm), n_D^{20} 1.5323, d_4^{20} 1.0550, MR_D 71.80. $C_{12}H_{20}OS_2F_2$. Calculated 72.06.

Found %: S 25.63, 25.67. $C_{12}H_{20}OS_2$. Calculated %: S 26.23.

Mercuric chloride complex: prepared by mixing solutions of the bis-sulfide and mercuric chloride in anhydrous acetone; the precipitate was washed with anhydrous acetone and ether; decomp. p. 120-125°.

Found %: Hg 50.66, 50.71. $C_{12}H_{20}OS_2Cl_4Hg_2$. Calculated %: Hg 50.95.

b) 2,5-Bis(isobutylmercaptomethyl)furan. From 9 g (0.1 mole) of isobutylmercaptan and 6.6 g (0.04 mole) of (I) was obtained 8.5 g (77%).

B.p. 155-156° (2mm), n_D^{20} 1.5213, d_4^{20} 1.0229, MR_D 81.16. $C_{14}H_{24}OS_2F_2$. Calculated 81.30.

Found %: C 61.85, 61.97; H 8.47, 8.54; S 23.63, 23.86. $C_{14}H_{24}OS_2$. Calculated %: C 61.70; H 8.88; S 23.54.

Mercuric chloride complex: decomp. p. 140–144°.

Found %: Hg 48.87, 49.00. $C_{14}H_{24}OS_2Cl_4Hg_2$. Calculated %: Hg 49.20.

c) 2,5-Bis(isoamylmercaptomethyl)furan. From 10.4 g (0.1 mole) of isoamylmercaptan and 6.6 g (0.04 mole) of (I) was obtained 9.6 g (80%).

B.p. 159–160° (1 mm), n_D^{20} 1.5140, d_4^{20} 1.0030, MR_D 90.17. $C_{16}H_{28}OS_2F_2$. Calculated 90.54.

Found %: S 21.16, 21.23. $C_{16}H_{28}OS_2$. Calculated %: S 21.34.

d) 2,5-Bis(n-nonylmercaptomethyl)furan. From 16 g (0.1 mole) of n-nonylmercaptan and 6.6 g (0.04 mole) of (I) was obtained 14.1 g (86%); m.p. 36–37° (from alcohol).

Found %: S 15.25, 15.33. $C_{24}H_{44}OS_2$. Calculated %: S 15.54.

e) 2,5-Bis(benzylmercaptomethyl)furan. A. from 12.4 g (0.1 mole) of benzylmercaptan and 6.6 g (0.04 mole) of (I) was obtained 11.55 g (85%); m.p. 44–45° (from ligroine).

Found %: S 18.45, 18.56. $C_{20}H_{20}OS_2$. Calculated %: S 18.83.

B. From 0.7 g (0.0044 mole) of 2,5-bis(mercaptomethyl)furan, 0.02 g (0.0088 g-atom) of sodium and 1.1 g (0.0088 mole) of benzyl chloride was obtained 1 g (67%); m.p. 43–44° (from ligroine). No depression in admixture with the preceding preparation.

f) 2,5-Bis(furfurylmercaptomethyl)furan. A. From 11.4 g (0.1 mole) of furfurylmercaptan [4] and 6.6 g (0.04 mole) of (I) was obtained 11.4 g (89%); m.p. 66–67° (from ligroine).

Found %: S 19.80, 19.90. $C_{16}H_{16}O_3S_2$. Calculated %: S 20.01.

B) From 0.5 g (0.003 mole) of 2,5-bis(mercaptomethyl)furan, 0.014 g (0.006 g-atom) of sodium and 0.7 g (0.006 mole)of furfuryl chloride [5] was obtained 0.7 g (70%); m.p. 65–66° (from ligroine). No melting point depression was observed in admixture with the preceding preparation.

g) 2,5-Bis(β-piperidylethylmercaptomethyl)furan. From 14.5 g (0.01 mole) of β-piperidylethylmercaptan and 6.6 g (0.04 mole) of (I) was obtained 11.0 g (72%) of a dark oil.

The dihydrochloride was obtained by passage of dry hydrogen chloride into its etheral solution; no change on heating to 300°.

Found %: S 14.08, 14.13; Cl 15.51, 15.60. $C_{20}H_{36}ON_2S_2Cl_2$. Calculated %: S 14.07; Cl 15.55.

Dipicrate: prepared by mixing chloroform solutions of bisaminosulfide and picric acid; m.p. 142–143° (from glacial acetic acid).

Found %: S 7.62, 7.63. $C_{32}H_{42}O_{15}N_8S_2$. Calculated %: S 7.62.

h) 2,5-Bis(phenylmercaptomethyl)furan. From 11 g (0.1 mole) of thiophenol and 6.6 g (0.04 mole)of (I) was obtained 7.5 g (60%).

B.p. 191–192° (1.5 mm), n_D^{20} 1.6283, d_4^{20} 1.2015, MR_D 92.32. $C_{18}H_{16}OS_2F_3$. Calculated 92.57.

Found %: S 20.75, 20.77. $C_{18}H_{16}OS_2$. Calculated %: S 20.52.

SUMMARY

Starting from 2,5-bis(chloromethyl)furan, the following new compounds were synthesized: 2,5-bis(mercaptomethyl)furan, 2,5-bis(alkoxymethyl)furans, also 2,5-bis(alkylmercaptomethyl)- and 2,5-bis(arylmercaptomethyl)-furans.

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*Original Russian pagination. See C. B. translation.

THE CHEMISTRY OF SELENOPHENE

XXVII. COMPOSITION OF THE PRODUCT OF NITRATION OF SELENOPHENE

Yu. K. Yur'ev, E. L. Zaitseva, and G. G. Rozantsev

Moscow State University

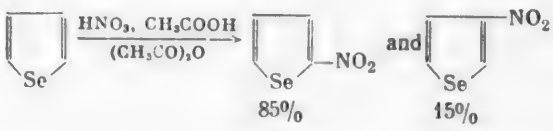
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2207-2209, July, 1960
Original article submitted July 1, 1959

In our preceding communication [1] we showed that nitroselenophene, obtained by Umezawa [2] by nitration of selenophene and described by him as 2-nitroselenophene, is actually a mixture of 3-nitroselenophene (70%) and 2-nitroselenophene (30%). However, the formation during nitration of selenophene of a mixture of mononitro compounds containing over twice as much β-isomer as α-isomer conflicts with the theoretically based conclusions, which are supported by numerous experimental facts, concerning the higher electronic density at α-sites in comparison with β-sites in five-membered heterocyclic compounds of an aromatic character – furan and thiophene as well as selenophene (their isolog). For example, the nitration of furan [3] with fuming nitric acid in a medium of acetic anhydride leads exclusively to 2-nitrofuran; nitration of thiophene under similar conditions [4, 5] gives 2--nitrothiophene together with only 5% of 3-nitrothiophene.

In the light of these facts we must assume that nitration of selenophene gives predominantly 2-nitroselenophene, i.e., the α-form; the subsequent working-up of the crude product with the aim of separation of the lower melting and more soluble α-form, involving numerous recrystallizations, results in more of the α-form being lost than the β-form (i.e., 3-nitroselenophene). Losses of the α-form and accumulation of β-form in the crystals continue until the two isomers start to crystallize out together in the ratio indicated above.

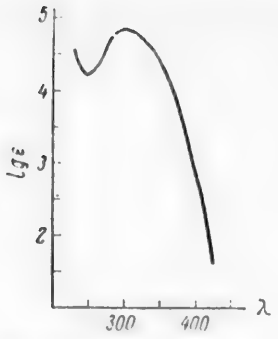
For further proof of the correctness of this conclusion, we studied the ultraviolet absorption spectra of the individual nitro compounds – 2-nitro- and 3-nitroselenophenes [1], prepared by decarboxylation of the acids, and also of the product of nitration of selenophene obtained by Umezawa's method [2]. The latter preparation was only distilled with steam (for separation from resins) and then totally distilled in vacuo (after removal of traces of unchanged selenophene by distillation).

Comparison of the UV absorption curves of pure mononitroselenophenes [1] and of the product of nitration of selenophene (diagram) confirmed our ideas and showed that the latter is a mixture of mononitroselenophenes in which the α-isomer indeed predominates: the content of 2-nitroselenophene is 85%, while that of 3-nitroselenopene is only 15%.



The absorption curve of this mixture of products of nitration of selenophene coincides with the absorption curve of an artificially prepared mixture of isomeric nitroselenophenes of the same composition.

We may note that an improvement of the technique of separation of products of nitration of selenophene from the reaction mixture enabled us to raise the yield of nitroselenophenes from 15 to 25%. A further crop of



UV spectrum of product of nitration of selenophene not subjected to crystallization (mixture of 85% of 2-nitroselenophene and 15% of 3-nitroselenophene).

nitro products could be isolated by ether extraction of the acid solution remaining after separation of the organic layer. Attempts at further increase in yield, however, are evidently complicated by the considerable resinification of the substance during the reaction.

Comparison of the results of nitration of furan, thiophene and selenophene consequently shows that in the nitration of the unsubstituted selenophene nucleus there is a more marked decrease in the influence of the heteroatom directing an entering electrophilic substituent into the α-position of the ring. The influence of the heteroatom declines in the order furan > thiophene > selenophene. As pointed out previously [1], this is undoubtedly associated with the fall of electronegativity in transition from oxygen to sulfur and then to selenium, and with the resulting increased polarizability of these atoms.

EXPERIMENTAL

A solution of 4 ml of fuming nitric acid (d 1.5) in 40 ml of glacial acetic acid was slowly added dropwise with vigorous stirring to 8.2 g (0.07 mole) of selenophene in 26 ml of acetic anhydride, the temperature of the mixture being held at -4 to -5°. The reaction mixture was then stirred at this temperature for another 20 min and poured into 300 ml of iced water. After the oily layer had been separated, the acid layer was extracted with ether. The mixture of ether extracts and oily layer was washed with dilute sodium bicarbonate solution and with water. After the ether had been distilled off, the residue was distilled with steam, the distillate extracted with ether and the ether extracts dried with sodium sulfate.

After the ether had been distilled off, the residue was distilled in vacuo. The whole mixture of α- and β-nitroselenophenes came over in the 76–87° (5 mm) range, the main bulk coming over at 76–78° and a smaller fraction at 86–87° (5 mm), i.e., two conspicuous temperature plateaus were observed.

There was obtained 2.75 g (25%) of a mixture of mononitroselenophenes in the form of a yellow oil permeated with acicular crystals. A sample was taken from the melt for determination of the selenium content.

Found %: Se 44.62, 44.55. $C_4H_3O_2NSe$. Calculated %: Se 44.85.

The ultraviolet absorption spectra were obtained with a SF-4 spectrophotometer with nonautomatic recording, using quartz cells and a hydrogen lamp. The solvent was methanol and the concentration (moles × l^{-1}) = 10^{-4}. The spectroscopic samples were taken from a melt of the prepared mixture of mononitroselenophenes.

Absorption maximum	3-Nitroselenophene	Mixture of 70% of 3-nitroselenophene and 30% of 2-nitroselenophene		Mixture of 85% of 2-nitroselenophene and 15% of 3-nitroselenophene		2-Nitroselenophene
		preparation obtained by Umezawa's method (i.e. after crystallization)	artificial mixture	product of nitration of selenophene	synthetic mixture	
mμ	290	295	294	298	298	300
ε α	6770	7245	7262	7244	7328	7480

SUMMARY

Nitration of selenophene by fuming nitric acid in acetic anhydride yields a mixture of mononitroselenophenes. When purified solely by distillation with steam in vacuo, this mixture contains 85% of 2-nitroselenophene and 15% of 3-nitroselenophene.

Crystals isolated from the mixture (by cooling), and then recrystallized, melt at 45–47° and contain 30% of 2-nitroselenophene and 70% of 3-nitroselenophene. This change is due to losses of the α-isomer which "fails to crystallize" owing to its lower melting point and greater solubility.

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*Original Russian pagination. See C. B. translation.

THE CHEMISTRY OF SELENOPHENE

XXVIII. REACTIONS OF 4-NITRO- AND 5-NITRO-2-ACETOSELENOPHENES

Yu. K. Yur'ev, E. L. Zaitseva, and A. N. Nikiforova

Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2209-2214, July, 1960
Original article submitted July 10, 1959

In preceding papers [1, 2] we described the preparation of 5-nitro-2-acetoselenophene (by reaction of 5-nitroselenophene-2-carboxylic acid chloride with ethoxymagnesium malonic ester) and of 4-nitro-2-acetoselenophene (by nitration of 2-acetoselenophene with nitrating mixture). The present work is concerned with the synthesis of derivatives of these nitroselenophene ketones.

5-Nitro-2-acetoselenophene was made to condense with various hydrazine derivatives by the procedure described previously for the analogous condensation of 5-nitroselenophene-2-aldehyde [3].

$R = -NHC_6H_5$, $-C_5H_4N$, $-C_4H_3O$, $-CH_2CN$.

We prepared the 4-phenylsemicarbazone (96%), isonicotinoylhydrazone (60%), furoylhydrazone (33.5%) and cyanoacetylhydrazone (83.5%) of 5-nitro-2-acetoselenophene.

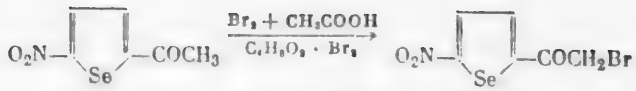
The slightly lower yields of hydrazones of the nitroketone in comparison with those of hydrazones of 5-nitroselenophene-2-aldehyde (90-100%) is evidently due to the lower reactivity of 5-nitro-2-acetoselenophene.

Bromination of 4-nitro- and 5-nitro-2-acetoselenophenes was effected with bromine in glacial acetic acid and with dioxane dibromide.

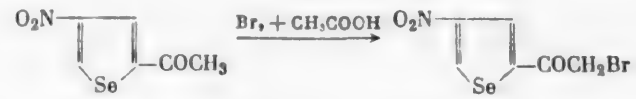
Concerning the bromination of isologs of 5-nitro-2-acetoselenophene, we know that 5-nitro-2-bromoacetylfuran (57%) was obtained by Dann et al. [4] by the action of bromine in glacial acetic acid on 5-nitro-2-acetylfuran; bromination of 5-nitro-2-acetylfuran with dioxane dibromide enabled N.O. Saldabol [5] to raise the yield of α-bromoketone to 87%. By a similar procedure Carrara and Weitnauer [6] succeeded in obtaining 5-nitro-2-bromoacetothiophene in a yield of nearly 100%.

We obtained 5-nitro-2-acetoselenophene in 73.5% yield by the action of bromine in glacial acetic acid on 5-nitro-2-bromoacetoselenophene at 80°. However in spite of the reaction being conducted in a nitrogen stream, the bromoketone still contained resinous impurities and apparently some dibromide.

Bromination of the nitroketone with dioxane dibromide at room temperature enabled 5-nitro-2-bromoacetoselenophene to be obtained in fairly high purity in 80% yield.

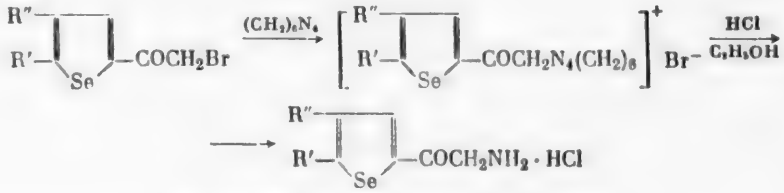


An attempt to brominate 4-nitro-2-acetoselenophene with dioxane dibromide was unsuccessful, the ketone being recovered unchanged. Bromination was effected with bromine in glacial acetic acid, and pure 4-nitro-2-bromoacetoselenophene was obtained in 85.5% yield.



It is evidently more resistant than 5-nitro-2-bromoacetoselenophene to the action of hydrogen bromide. The hydrogen atoms of the 5-nitro compound at the α-carbon atom are more labile.

We brought 4-nitro- and 5-nitro-2-bromoacetoselenophene into reaction with hexamethylenetetramine in order to obtain the corresponding aminoketones of the selenophene series.

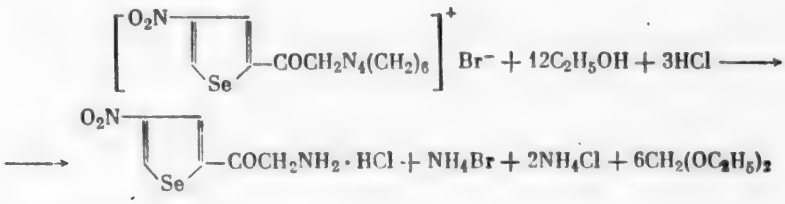


1) $R' = NO_2$, $R'' = H$; 2) $R' = H$, $R'' = NO_2$.

In the first step of this synthesis the complex of 4-nitro-2-bromoacetoselenophene with hexamethylenetetramine is obtained smoothly (73%) by mixing equimolar quantities of reactants in chloroform and standing the mixture for two days at room temperature. This procedure was not altogether successful for preparation of the complex of 5-nitro-2-acetoselenophene with hexamethylenetetramine, the yield not exceeding 38%. We then carried out the reaction in dry chlorobenzene at 50°, using the procedure described for preparation of the corresponding complex of p-nitro-α-bromoacetophenone [7], and obtained the hexamethylenetetramine complex of 5-nitro-2-bromoacetoselenophene in 83% yield.

It is interesting to note that Dann et al. [4], likewise Belinghi et al. [8], obtained the complex of 4-nitro-2-bromoacetothiophene with hexamethylenetetramine in a yield of 77 and 85% respectively by standing a mixture of equimolar quantities of reactants in chloroform at room temperature for 12-14 hr. Carrara and Weitnauer [6] were only able to obtain the complex of 5-nitro-2-bromoacetothiophene with hexamethylenetetramine by heating an equimolar mixture of the components in chlorobenzene.

The hexamethylenetetramine-4-nitro-2-bromoacetoselenophene complex was smoothly hydrolyzed by treatment with a mixture of alcohol and concentrated hydrochloric acid (2 : 1 by volume) in the cold for 48 hr (the procedure described for hydrolysis of the hexamethylenetetramine–p-nitro-α-bromoacetophenone complex [7]).



The resulting hydrochloride of the nitroaminoketone is always contaminated with ammonium salts. We therefore isolated 4-nitro-2-aminoacetoselenophene in the form of its acetyl derivative (73% calculated on the complex); hydrolysis of the acetyl derivative gave the pure hydrochloride of the nitroaminoketone (92%). An attempt to apply

this procedure to the preparation of 5-nitro-2-aminoacetoselenophene was unsuccessful. Hydrolysis of the hexamethylenetetramine–5-nitro-2-bromoacetoselenophene complex could only be brought to successful completion if we considerably reduced the hydrochloric acid concentration in the alcohol (to 1:8 by volume) and distilled off the resulting diethylformal. Three additions of fresh acid were made and diethylformal was distilled off after each addition. We acetylated the resulting 5-nitro-2-aminoacetoselenophene hydrochloride and obtained 5-nitro-2-acetylaminoacetoselenophene (32%).

In the unsuccessful experiments on hydrolysis of the hexamethylenetetramine complex, condensation evidently took place between the formaldehyde (formed in the reaction) and the aminoketone with formation of the N-methyleneimine which is cleaved with great difficulty. A higher concentration of alcohol diminished the possibility of formation of 5-nitro-2-(N-methyleneimino) acetoselenophene. If under these conditions it is nevertheless still formed to a small extent, then the above-described repeated treatment with a mixture of alcohol and concentrated hydrochloric acid should result in its cleavage.

The nitro group in the 5 position consequently exerts a marked influence on the reactivity of 5-nitro-2-selenophene and its derivatives obtained by replacement of the hydrogen of the α-carbon atom by bromine or an amino group.

To account for this influence, we may assume that the electron-capturing action of the nitro group is more effectively transmitted by the selenophene ring from the α'-position than from the β'-position due to the ability of this ring to behave like a conjugated system of double bonds.

EXPERIMENTAL

1. Derivatives of 5-Nitro-2-acetoselenophene

a) 4-Phenylsemicarbazone of 5-nitro-2-acetoselenophene. A mixture of 0.42 g of 5-nitro-2-acetoselenophene (m.p. 120–121° [1]) in 7 ml of alcohol and 0.4 g of 4-phenylsemicarbazide hydrochloride in 1.2 ml of water was heated for 15 min. It was then cooled and 8 ml of water was added. Yield 0.61 g (95.5%); m.p. 253–254° (decomp., from alcohol); yellow crystals.

Found %: C 44.28, 44.33; H 3.06, 3.04; Se 22.40, 33.28. $C_{13}H_{12}O_3N_4Se$. Calculated %: C 44.44; H 3.41; Se 22.51.

b) Isonicotinoylhydrazone of 5-nitro-2-acetoselenophene. After 0.42 g of nitroketone and 0.27 g of isonicotinoylhydrazide in 12 ml of alcohol had been boiled for 5 hr, the mass was cooled and 7 ml of water was added. The mixture was stood for 3 hr. The precipitate was washed with water and ether. After evaporation of the ether, 0.15 g of unchanged ketone was recovered. Yield 0.4 g (approx. 100% calculated on the nitroketone used); m.p. 257–258° (decomp., from alcohol); yellow crystals.

Found %: C 42.59, 42.53; H 3.01, 2.82; Se 23.21, 23.24. $C_{12}H_{10}O_3N_4Se$. Calculated %: C 42.73; H 2.96; Se 23.44.

c) Cyanoacetylhydrazone of 5-nitro-2-acetoselenophene. To 0.2 g of cyanoacetic acid hydrazide in 5.6 ml of alcohol, acidified with 1 ml of concentrated hydrochloric acid, was added dropwise with stirring 0.42 g of the nitroketone in 7 ml of alcohol; the mass was then stood for 12 hr at 20° and 11 ml of water was added. The precipitate was washed with water and ether. Yield 0.5 g (83.5%); m.p. 258–259° (decomp., from alcohol); yellow crystals.

Found %: C 35.77, 35.86; H 2.55, 2.45; Se 26.29, 26.25. $C_9H_8O_3N_4Se$. Calculated %: C 36.14; H 2.69; Se 26.42.

d) Furoylhydrazone of 5-nitro-2-acetoselenophene. By the same procedure as under a), 0.42 g of nitroketone and 0.26 g of furoyl hydrazide gave 0.22 g (33.5%); m.p. 266–267° (decomp., from alcohol); yellow crystals.

Found %: C 40.37, 40.43; H 2.65, 2.83; Se 24.25, 24.30. $C_{11}H_9O_4N_3Se$. Calculated %: C 40.50; H 2.78; Se 24.28.

e) Thiosemicarbazone of 5-nitro-2-acetoselenophene. A mixture of 0.4 g of nitroketone and 0.16 g of thiosemicarbazide in 2.7 ml of alcohol was acidified with two drops of glacial acetic acid and boiled for an hour, cooled and poured into cold water. Yield 0.44 g (84.5%); m.p. 235–236° (decomp., from alcohol); orange crystals.

Found %: C 31.37, 31.34; H 2.93, 2.88. $C_7H_5O_2N_4SSe$. Calculated %: C 31.00; H 2.97.

5-Nitro-2-bromoacetoselenophene. a) Into a solution of 1 g of nitroketone in 20 ml of dioxane was stirred 1.27 g of dioxan dibromide in the course of 0.5 hr. The mass was stood for 12 hr and poured into 20 ml of cold water. Yield 1.08 g (80%); m.p. 125.5–126° (from ligroine); yellow crystals.

b) To 1 g of nitroketone in 10 ml of glacial acetic acid was added dropwise with stirring 0.9 g of bromine in 5.6 ml of glacial acetic acid in the course of an hour. The solution, colored by bromine, was heated at 80° for 40 min in a gentle stream of nitrogen until the color had disappeared; the light-yellow mixture was then poured into 65 ml of iced water. Yield 1.02 g (76%); m.p. 125.5–126° (from ligroine).

Found %: C 24.13, 24.18; H 1.27, 1.30; Se 26.47, 26.50. $C_6H_4O_3NBrSe$. Calculated %: C 24.26; H 1.36; Se 26.53.

Complex of 5-nitro-2-bromoacetoselenophene with hexamethylenetetramine. In a three-necked flask, fitted with stirrer, thermometer and dropping funnel, were placed 0.26 g of hexamethylenetetramine and 18 ml of chlorobenzene. To the resulting suspension was added a warm solution of 0.5 g of nitroketone in 1.8 ml of chlorobenzene. The mixture was stirred for 5 hr in the dark at 50° and stood for 12 hr at 20°. The precipitate was washed with anhydrous alcohol and ether. Yield 0.65 g (83%); m.p. 125–128° (decomp.); yellow crystals, darkening in the light and decomposing when heated.*

5-Nitro-2-acetylaminoacetoselenophene. The complex (0.6 g) was stirred for 15 min at 20° with a mixture of 0.6 ml of 38% hydrochloric acid and 4.8 ml of alcohol (the temperature of the mixture rose to 33-35°), the mass was stood for a day and the liquid portion evaporated to dryness in vacuo. Addition was then made of 4.8 ml of alcohol and 0.6 ml of concentrated hydrochloric acid. On the following day the evaporation to dryness in vacuo was repeated. This operation was repeated once more. The residue was triturated with absolute ether (5 ml). There was obtained 0.68 g of 5-nitro-2-aminoacetoselenophene hydrochloride in admixture with ammonium salts.

This mixture was dissolved in 2.5 ml of water and the solution was filtered. Rapid addition was then made (with vigorous stirring and cooling with ice and salt) of 0.26 ml of acetic anhydride followed by 0.22 g of sodium acetate in 0.9 ml of water. Stirring was continued for another 0.5 hr at 20°. The product was acidified with hydrochloric acid and cooled to 0°; the precipitate was filtered off and washed with water. Yield 0.12 g (32% calculated on the complex); m.p. 165–166° (decomp.; after reprecipitation with ligroine from ethyl acetate); yellow crystals.

Found %: C 35.18, 35.17; H 3.08, 3.13; Se 28.58, 28.55. $C_8H_6O_4N_2Se$. Calculated %: C 34.93; H 2.93; Se 28.74.

2. Derivatives of 4-nitro-2-acetoselenophene

4-Nitro-2-bromoacetoselenophene. To 0.93 g of 4-nitro-2-acetoselenophene (m.p. 122.5–123.5° [2]) in 9 ml of glacial acetic acid was added dropwise with stirring 0.7 g of bromine in 5 ml of glacial acetic acid in the course of an hour. The solution (colored by bromine) was heated for 40 min at 80° in a gentle nitrogen stream until the color disappeared, and the light-yellow mixture was run into 60 ml of iced water. The precipitate was washed with water. Yield 1.08 g (85.5%); m.p. 103–104° (from alcohol); white crystals.

Found %: C 24.32, 24.46; H 1.34, 1.42; Se 26.48, 26.63. $C_6H_4O_3NBrSe$. Calculated %: C 24.26; H 1.36; Se 26.58.

Complex of 4-nitro-2-bromoacetoselenophene with hexamethylenetetramine. A solution of 0.21 g of hexamethylenetetramine in 4 ml of chloroform was mixed with 0.4 g of nitroketone in 3 ml of chloroform. The mixture was stood in the dark for two days. The white precipitate was filtered and washed with a little chloroform. Yield 0.45 g (73%); m.p. 155–156° (decomp.); white crystals, rapidly turning red in the light and decomposing when heated.*

4-Nitro-2-acetylaminoacetoselenophene. A mixture of 1.8 ml of concentrated hydrochloric acid and 3.6 ml of alcohol was stirred with 0.9 g of complex at 20° until the precipitate dissolved completely (15 min). The mass was stood for two days. It was then cooled to 0°, and the precipitate was filtered and washed with ether. Yield 0.6 g of 4-nitro-2-acetylaminoacetoselenophene hydrochloride in admixture with ammonium salts. After this mixture had been dissolved in 2.2 ml of water, rapid addition was made (with vigorous stirring and cooling with ice and salt) of 0.4 ml of acetic anhydride. This was followed by 0.34 g of sodium acetate in 1.4 ml of water, and stirring was continued

* Analysis of the complex was impossible for this reason.

for another 0.5 hr at 20°. After acidification with hydrochloric acid, the precipitate was filtered and washed with water. Yield 0.4 g (70.5% reckoned on the complex); m.p. 188–189° (decomp., from alcohol); white crystals.

Found %: C 34.65, 34.54; H 3.02, 2.96; Se 28.45, 28.36. $C_8H_8O_4N_2Se$. Calculated %: C 34.93; H 2.93; Se 28.74.

4-Nitro-2-aminoacetoselenophene hydrochloride. 4-Nitro-2-acetylaminoacetoselenophene (0.2 g) was boiled for 20 min with 1 ml of 18% hydrochloric acid. The mass was evaporated to dryness. Yield 0.18 g (92%); m.p. 225–226° (decomp., after reprecipitation with ether from absolute alcohol); white crystals.

Found %: C 26.55, 26.38; H 2.48, 2.40; Se 29.14, 29.10. $C_6H_7O_3N_2ClSe$. Calculated %: C 26.75; H 2.59; Se 29.29.

SUMMARY

1. Condensation with hydrazine derivatives gave isonicotinoyl-, cyanoacetyl- and furoylhydrazones of 5-nitro-2-acetoselenophene; the 4-phenylsemicarbazone of 5-nitro-2-acetoselenophene was also prepared.

2. It was shown that 4-nitro-2-acetoselenophene is brominated under more drastic conditions than 5-nitro-2-acetoselenophene, due to the greater mobility of the hydrogen atoms at the α-carbon atom of the acetyl group of 5-nitro-2-acetoselenophene.

3. 4-Nitro-2-bromoacetoselenophene forms a complex with hexamethylenetetramine with greater facility than does 5-nitro-2-bromoacetoselenophene. Hydrolysis of these complexes and subsequent acetylation leads to 4-nitro- and 5-nitro-2-acetylaminoacetoselenophene.

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4-METHYLENE-2,2,5,5-TETRAMETHYL-3-FURANIDONE

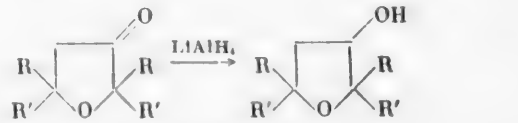
I. K. Korobitsyna, Yin Ch'ên-Lieh, and Yu. K. Yur'ev

Moscow State University

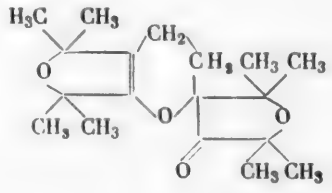
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2214-2218, July, 1960
Original article submitted July 10, 1959

Continuing our work on reactions of ketones of the tetrahydrofuran series, we prepared the simplest vinyl ketone of this series—4-methylene-2,2,5,5-tetramethyl-3-furanidone. Since one of the routes to this substance could be reduction with lithium aluminum hydride of 4-hydroxymethylene-2,2,5,5-tetramethyl-3-furanidone (previously described by us [1]), it was necessary to first clarify the behavior of 2,2,5,5-tetraalkyl-3-furanidones themselves, especially since this problem has been the subject of only one investigation [2].

We established that lithium aluminum hydride in ethereal solution smoothly reduces 2,2,5,5-tetraalkyl-3-furanidones to 2,2,5,5-tetramethyl-3-furanidols in high yields (83-98%) which are better than those obtained by reduction with sodium in alcohol [3] or with hydrogen in presence of skeletal nickel. [4].

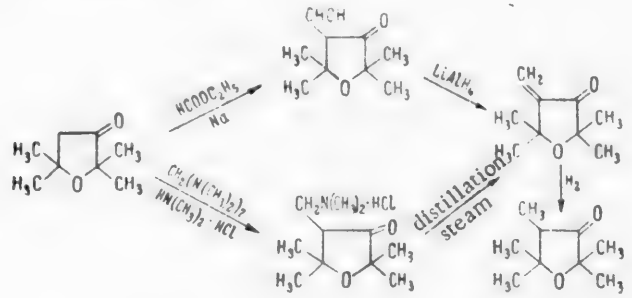


Reduction of 4-hydroxymethylene-2,2,5,5-tetramethyl-3-furanidone by lithium aluminum hydride takes a different course; unlike hydroxymethylene ketones of the alicyclic series—which on reduction with lithium aluminum hydride in the majority of cases form a mixture of unsaturated alcohols [5]—it gives the unsaturated ketone, 4-methylene-2,2,5,5-tetramethyl-3-furanidone, in a yield of 61% (calculated on the hydroxymethylene ketone brought into reaction) when isolated in the form of the dibromide. It is impossible, however, to isolate the free 4-methylene-2,2,5,5-tetramethyl-3-furanidone in sufficiently high yield since it dimerizes to a considerable extent in the course of fractional distillation; dimerization is extremely facile in presence of acids and alkalies. On the analogy of o-methylenecyclohexanone [6] we assume that the dimer of 4-methylene-2,2,5,5-tetramethyl-3-furanidone is formed by a "dienic synthesis" and has the following structure:



Hydrogenation of 4-hydroxymethylene-2,2,5,5-tetramethyl-3-furanidone in presence of various catalysts (skeletal nickel, platinum oxide, palladium oxide on barium sulfate and platinum oxide in presence of salts of trivalent iron) gives only low yields (5-23%) of 4-methylene-2,2,5,5-tetramethyl-3-furanidone.

Another route leads to better results. Reaction of 2,2,5,5-tetramethyl-3-furanidone with tetramethylmethylenediamine and dimethylamine hydrochloride gives the hydrochloride of the Mannich base—4-dimethylaminomethylene-2,2,5,5-tetramethyl-3-furanidone—in a yield of 55.7%. Steam distillation of the latter leads to 4-methylene-2,2,5,5-tetramethyl-3-furanidone in a yield of 95.5%.



We may note that attempts to prepare the Mannich bases by the action of formalin and diethylamine hydrochloride on 2,2,5,5-tetramethyl-3-furanidone gave negative results.

We obtained 2,2,4,5,5-pentamethyl-3-furanidone by hydrogenation of 4-methylene-2,2,5,5-tetramethyl-3-furanidone in presence of palladium on barium sulfate.

EXPERIMENTAL

1. Reduction of 2,2,5,5-Tetraalkyl-3-furanidones by Lithium Aluminum Hydride

a) 2,2,5,5-Tetramethyl-3-furanidone. Dropwise addition of 100 ml of an ethereal solution of lithium aluminum hydride [from 14 g (0.053 mole) of aluminum bromide and 1.6 g (0.2 mole) of lithium hydride] with ice-cooling was made to a solution of 15 g (0.106 mole) of 2,2,5,5-tetramethyl-3-furanidone in 100 ml of absolute ether in a three-necked flask fitted with stirrer, dropping funnel and reflux condenser. The mixture was stirred for 3 hr at 18°, stood for 12 hr, decomposed with 2 N hydrochloric acid and extracted a number of times with ether. After the ether had been distilled off from the solution (previously dried with magnesium sulfate), the residue was distilled in vacuo to give 14.2 g (92%):

B.p. 84–84.5° (13 mm), m.p. 26.5–27°.

Found %: C 66.40, 66.30; H 11.22, 11.25. $C_8H_{16}O_2$. Calculated %: C 66.62; H 11.19.

Phenylurethane: m.p. 123–124° (from ligroine).

Found %: N 5.61, 5.56. $C_{15}H_{21}O_3N$. Calculated %: N 5.34.

Literature data [3]: b.p. 84° (15 mm), n^{17} 1.4435, d^{17} 0.9483; phenylurethane m.p. 123°.

b) 2,5-Dimethyl-2,5-diethyl-3-furanidone. As described above, from 17 g (0.1 mole) of 2,5-dimethyl-2,5-diethyl-3-furanidone and 100 ml of ethereal solution of lithium aluminum hydride [from 13.5 g (0.05 mole) of aluminum bromide and 1.6 g (0.02 mole) of lithium hydride] was obtained 14.4 g (83.5%):

B. p. 101–101.5° (11 mm), n_D^{20} 1.4578, d_4^{20} 0.9520, MR_D 49.36; Calc. 49.35.

Found %: C 69.77, 69.84; H 11.72, 11.83. $C_{10}H_{20}O_2$. Calculated %: C 69.72; H 11.70.

3,5-Dinitrobenzoate: m.p. 89–90° (from ligroine).

Found %: N 8.04. $C_{17}H_{22}O_7N_2$. Calculated %: N 7.65.

Literature data [4]: b.p. 107° (19 mm), n_D^{15} 1.4547, d_{15} 0.9539, MR_D 48.90.

c) 2,2,5,5-Bistetramethylene-3-furanidol. By the above procedure, 19.4 g (0.1 mole) of 2,2,5,5-tetramethyl-3-furanidone and 100 ml of ethereal solution of lithium aluminum hydride [from 13.5 g (0.05 mole) of aluminum bromide and 1.6 g (0.2 mole) of lithium hydride] gave 17.1 g (86.5%):

B.p. 118–119° (3 mm), n_D^{20} 1.5011, d_4^{20} 1.0660, MR_D 54.23; Calc. 54.18.

Found %: C 73.11, 73.30; H 10.44, 10.33. $C_{12}H_{20}O_2$. Calculated %: C 73.45; H 10.27.

Phenylurethane: m.p. 86.5-87° (from ligroine).

Found %: N 4.38, 4.33. $C_{19}H_{25}O_3N$. Calculated %: N 4.44.

d) 2,2,5,5-Bispentamethylene-3-furanidol. Prepared in similar fashion from 15.8 g (0.07 mole) of 2,2,5,5-bispentamethylene-3-furanidone and 100 ml of ethereal solution of lithium aluminum hydride [prepared from 9.35 g (0.035 mole) of aluminum bromide and 1.1 g (0.14 mole) of lithium hydride].

Yield 15.3 g (98%); m.p. 72.5 -73.5° (from methyl alcohol).

Found %: C 75.23; 75.21; H 10.85; 10.78. $C_{14}H_{24}O_2$. Calculated %: C 75.12; H 10.79.

Phenylurethane: m.p. 123-124° (from alcohol).

Found %: N 4.02, 4.07. $C_{21}H_{29}O_3N$. Calculated %: N 4.08.

2. Reduction of 4-Hydroxymethylene-2,2,5,5-tetramethyl-3-furanidone with Lithium Aluminum Hydride

Reduction of 5.6 g (0.033 mole) of the hydroxymethylene ketone was effected as described above by 120 ml of ethereal solution of lithium aluminum hydride [from 10.5 g (0.04 mole) of aluminum bromide and 1.8 g (0.23 mole) of lithium hydride]. The mixture was stood for 12 hr, decomposed with a 2N hydrochloric acid and extracted with ether. The ether extracts were dried with magnesium sulfate. Two procedures for treatment of the residue after distillation of the ether were used: a) Bromine in carbon tetrachloride solution was added to the residue until the yellow color disappeared; removal of the solvent in vacuo left 6.3 g (60.8%) of the dibromide of 4-methylene-2,2, 5,5-tetramethyl-3-furanidone; m.p. 83.2-83.9° (from alcohol).

Found %: C 34.58, 34.61; H 4.67, 4.66; Br 50.68, 50.83. $C_9H_{14}O_2Br_2$. Calculated %: C 34.42; H 4.49; Br 50.88.

b) The residue was fractionated a number of times in vacuo to give 2 g of 4-methylene-2,2,5,5-tetramethyl-3-furanidone.

B.p. 75-77° (48 mm) n_D^{20} 1.4380, d_4^{20} 0.9357, MR_D 43.28. $C_9H_{14}O_2F$. Calculated 42.75.

Found %: C 69.75, 69.71; H 9.37, 9.17. $C_9H_{14}O_2$. Calculated %: C 70.10; H 9.16.

4-Methylene-2,2,5,5-tetramethyl-3-furanidone partly dimerizes during distillation, and the process is rapid in presence of dilute mineral acids and alkalies; the dimer is a white crystalline substance with m.p. 76-76.5° (from alcohol).

Found %: C 70.21, 70.11; H 9.28, 9.26. M 320.7. $(C_9H_{14}O_2)_2$. Calculated %: C 70.10; H 9.16. M 308.4.

3. 4-Methylene-2,2,5,5-tetramethyl-3-furanidone

A mixture of 28 g (0.2 mole) of 2,2,5,5-tetramethyl-3-furanidone, 22 g (0.22 mole) of tetramethylmethylenediamine, 16 g (0.2 mole) of dimethylamine hydrochloride and 100 ml of alcohol was boiled for 4 hr, the alcohol and unchanged substances were distilled off, and the residue was treated with 150 ml of 2 N sodium hydroxide and extracted with ether. Dry hydrogen chloride was passed through the ethereal solution. There was obtained 26.3 (55.7%) of 4-dimethylaminomethylene-2,2,5,5-tetramethyl-3-furanidone hydrochloride; m.p. 127-128° (after reprecipitation from absolute alcohol by absolute ether).

Found %: N 5.90, 5.94. $C_{11}H_{22}O_2NCl$. Calculated %: N 5.94.

The hydrochloride (26.3) was distilled with steam and the distillate extracted with ether. The extract was dried with magnesium sulfate, the ether distilled off, and the residue distilled in vacuo to give 16.4 (95.5%) of 4-methylene-2,2,5,5-tetramethyl-3-furanidone; b.p. 89-90° (73 mm), n_D^{20} 1.4370, d_4^{20} 0.9364.

Part of the 4-methylene-2,2,5,5-tetramethyl-3-furanidone dimerized at the close of distillation; m.p. 76-76.5°; a mixture with the dimer obtained in the preceding experiment melted without depression.

4-Methylene-2,2,5,5-tetramethyl-3-furanidone dibromide melts at 83-83.5°, and a mixture with the dibromide obtained in the preceding experiment melted without depression.

4. 2,2,4,5,5-Pentamethyl-3-furanidone

A solution of 10 g (0.065 mole) of 4-methylene-2,2,5,5-tetramethyl-3-furanidone in 25 ml of absolute alcohol was hydrogenated in the cold, with shaking, in presence of palladium on barium sulfate. After 104 min 1110 ml of hydrogen (NTP) had been absorbed (the calculated volume is 1455 ml at NTP). The catalyst was separated, the alcohol distilled off, and the residue distilled in vacuo. Yield 7.5 g (74.1%).

B.p. 52.53° (12 mm), n_D^{20} 1.4247, d_4^{20} 0.9166, MR_D 43.15; Calc. 43.37.

Found %: C 69.01, 69.17; H 10.66, 10.68. $C_9H_{16}O_2$. Calculated %: C 69.19; H 10.33.

2,4-Dinitrophenylhydrazone: m.p. 166.5-167° (from alcohol).

Found %: N 16.61, 16.96. $C_{15}H_{20}O_5N_4$. Calculated %: N 16.66.

SUMMARY

Reduction by lithium aluminum hydride of 2,2,5,5-tetraalkyl-3-furanidones can serve as a convenient method of synthesis of the corresponding alcohols.

4-Methylene-2,2,5,5-tetramethyl-3-furanidone is easily prepared by steam distillation of the hydrochloride of the Mannich base formed from 2,2,5,5-tetramethyl-3-furanidone, tetramethylmethylenediamine and dimethylamine hydrochloride.

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ORGANOPHOSPHORUS INSECTICIDES

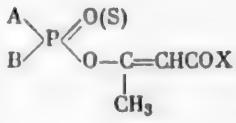
DERIVATIVES OF β-DICARBONYL COMPOUNDS

M. I. Kabachnik, P. A. Rossiiskaya, M. P. Shabanova, D. M. Patkin,

L. F. Efimova, and N. M. Gamper

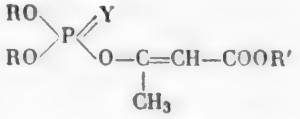
Institute of Heteroorganic Compounds, Academy of Sciences, USSR
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2218-2223,
July, 1960
Original article submitted June 19, 1959

For the purpose of systematic investigation of the insecticidal properties of derivatives of phosphoric and thiophosphoric acids possessing phosphorylating properties, we synthesized and studied the toxicity to insects of a series of esters of phosphorus acids and of the enolic forms of β-dicarbonyl compounds with the general formula:



where A and B are alkoxy- and dialkylamido groups, and X is alkyl or alkoxyl.

G. Schrader's survey [1] mentions two preparations (I and II) obtained by the action of diethyl chlorophosphate or diethyl chlorothiophosphate on the sodium derivative of methyl acetoacetate.



(I) $R = C_2H_5$, $R' = CH_3$, $Y = O$;
(II) $R = C_2H_5$, $R' = CH_3$, $Y = S$;
(III) $R = C_2H_5$, $R' = C_2H_5$, $Y = O$;
(IV) $R = CH_3$, $R' = CH_3$, $Y = O$.

Corresponding derivatives of ethyl acetoacetate (III) are known [2], as well as dimethyl (carbomethoxyisopropenyl)phosphate (IV) [3], marketed as "Shell OS-2046". This compound is reported to be a strong systemic poison comparable with "Systox" or OMPA. Two geometrical isomers of OS-2046 have been described [4], the cis-isomer being 100 times more toxic to insects and warm-blooded animals than the trans-isomer.

Kreytzkamp and Kayser [5] studied the reaction of triethyl phosphite with α-chloroacetoacetic ester and showed that diethyl (carbethoxyisopropenyl)phosphate is formed (III).

$$(C_2H_5O)_3P + CH_3COCHClCOOC_2H_5 \longrightarrow (C_2H_5O)_2P(O)OC(CH_3)=CHCOOC_2H_5 + C_2H_5Cl$$

This reaction was later also studied by Pudovik [6] and other workers [7,8].

We obtained esters of dialkylphosphoric acids and enolic forms of acetylacetone or acetoacetic ester by the action of dialkyl chlorophosphates on the corresponding β-dicarbonyl compounds in presence of a tertiary amine, under the conditions of Claisen O-acylation of β-dicarbonyl compounds.

TABLE 1.

Laboratory numbers	Formulas of substances	Boiling point (pressure in mm)	d^{20}_4	n_D^{20}	MR_D found	MR_D calculated
P-251	$(C_2H_5O)_2P(O)OC(CH_3)=CHCOOCH_3$	115—116 (0.5)	1.1615	1.4473	58.00	56.96
P-252	$(C_2H_5O)_2P(O)OC(CH_3)=CHCOCH_3$	113—115 (1.5)	1.1285	1.4458	55.75	55.30
P-255	$C_2H_5O[(CH_3)_2N]P(O)OC(CH_3)=CHCOOCH_3$	109—111 (1)	1.1415	1.4603	60.26	59.24
P-264	$C_2H_5O[(CH_3)_2N]P(O)OC(CH_3)=CHCOCH_3$	105—107 (1)	1.1271	1.4686	58.03	57.59
P-248	$(C_2H_5O)_2POC(CH_3)=CHCOOCH_3$	93—96 (3)	1.0778	1.4580	59.75	58.02
P-178	$(C_2H_5O)_2POC(CH_3)=CHCOCH_3$	85—87 (2)	1.0450	1.4620	57.88	56.43
P-256	$C_2H_5O[(CH_3)_2N]POC(CH_3)=CHCOOCH_3$	76—80 (0.5)	1.0620	1.4705	61.79	60.32
P-249	$C_2H_5O[(CH_3)_2N]POC(CH_3)=CHCOCH_3$	91—93	1.0540	1.4791	60.29	58.67
P-258	$[(CH_3)_2N]_2POC(CH_3)=CHCOOCH_3$	87—88 (0.5)	1.0420	1.4850	64.29	62.61
P-254	$(C_2H_5O)_2P(S)OC(CH_3)=CHCOOCH_3$	106—109 (1)	1.1614	1.4830	65.90	64.43
P-250	$(C_2H_5O)_2P(S)OC(CH_3)=CHCOCH_3$	92.5—93 (1)	1.1216	1.4807	63.90	62.79
P-257	$C_2H_5O[(CH_3)_2N]P(S)OC(CH_3)=CHCOOCH_3$	104—106 (0.5)	1.1456	1.4970	68.20	66.73
P-253	$C_2H_5O[(CH_3)_2N]P(S)OC(CH_3)=CHCOCH_3$	103—105 (1)	1.1121	1.4960	65.93	65.09
P-259	$[(CH_3)_2N]_2P(S)OC(CH_3)=CHCOOCH_3$	112—114 (0.5)	1.1381	1.5075	69.52	69.02
P-263	$(C_2H_5O)_2P(O)OC(Cl)(CH_3)CHClCOOCH_3$	143—146 (2)	1.3060	1.4591	67.62	67.15

$$\begin{matrix}RO\\RO\end{matrix}\!\!>\!P\!<\!\begin{matrix}O\\Cl\end{matrix} + CH_3COCH_2COX + R_3N \longrightarrow \begin{matrix}RO\\RO\end{matrix}\!\!>\!P\!<\!\begin{matrix}O\\OC(CH_3)=CHCOX\end{matrix} + R_3N\cdot HCl$$

We failed, however, to obtain derivatives of dialkylamidophosphoric acids by this method. On the other hand they are readily obtained by the method of Kreytzkamp and Kayser, for example:

$$\begin{matrix}C_2H_5O\\(CH_3)_2N\end{matrix}\!\!>\!P-OC_2H_5 + CH_3COCHClCOCH_3 =$$

$$= \begin{matrix}C_2H_5O\\(CH_3)_2N\end{matrix}\!\!>\!R\!<\!\begin{matrix}O\\O-C(CH_3)=CHCOCH_3\end{matrix} + C_2H_5Cl.$$

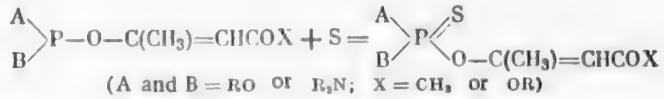
We synthesized derivatives of thiophosphoric acid containing alkoxyl or dialkylamido groups by a third route: starting from reaction of dialkyl chlorophosphites or the corresponding dialkylamido derivatives with β-dicarbonyl compounds under the conditions of Claisen acylation, we obtained derivatives of phosphorous acid:

$$\begin{matrix}A\\B\end{matrix}\!\!>\!P-Cl + CH_3COCH_2COX + R_3N = \begin{matrix}A\\B\end{matrix}\!\!>\!P-O-C(CH_3)=CHCOX + R_3N\cdot HCl.$$

(A and B = RO or R_2N; X = CH_3 or OR)

These are readily mobile liquids, distilling without decomposition in vacuo, soluble in organic solvents. They have an unpleasant odor. They easily add on sultur in carbon disulfide soltuion with formation of the sought-for derivatives of thiophosphoric acid.

Yield (in %)	% C		% H		% P		% S, Cl, N	
	found	calculated	found	calculated	found	calculated	found	calculated
72.2	42.91, 42.70	42.86	6.86, 6.67	6.75	12.33, 12.52	12.29	—	—
35.0	45.58, 45.41	45.76	7.43, 7.19	7.20	12.70, 12.93	13.13	—	—
22.0	43.31, 43.16	43.03	7.33, 7.38	7.17	12.27, 11.99	12.34	—	—
21.7	45.50, 45.72	45.96	7.75, 7.52	7.66	12.46, 12.60	13.18	—	—
58.2	—	—	—	—	13.30, 13.10	13.12	—	—
37.3	48.40, 48.48	49.09	7.72, 7,85	7.73	14.42, 14.58	14.11	—	—
51.9	45.38, 45.24	45.95	7.76, 7.79	7.66	12.86, 12.96	13.18	—	—
55.8	—	—	—	—	14.31, 14.36	14.14	6.41, 6.20	N 6.39
32.0	46.39, 46.41	46.15	8.43, 8,41	8.12	—	—	—	—
75.0	40.47, 40.44	40.30	6.37, 6.39	6.34	11.50, 11.53	11.57	11.55, 11.89	S 11.57
28.3	42.84, 42.85	42.86	6.78, 6.78	6.75	12.57	12.29	12.22, 12.29	S 12.70
66.2	40.56, 40.42	40.45	6.78, 6.75	6.74	11.36, 11.35	11.62	11.94, 11.96	S 11.98
41.6	43.05, 42.95	43.03	7.17, 7.17	7.17	12.47, 12.52	12.34	12.39, 12.21	S 12.75
42	40.94, 40.88	40.60	7.26, 7.27	7.14	11.79, 11.57	11.64	11.86, 12.00	S 12.03
70.1	33.38, 33.41	33.41	5.22, 5.24	5.25	9.87, 9.69	9.59	21.86, 22.11	Cl 21.97



(A and B = RO or R_2N; X = CH_3 or OR)

The ester of diethylphosphoric acid and of the enol form of methyl acetoacetate add on chlorine to give diethyl (carbomethoxydichloro-2-propyl)phosphate.

Constants and analyses of the prepared substances are set forth in Table 1.

The synthesized substances were examined in laboratory tests as contact and systemic poisons. Contact tests were made with the grubs of mealy bug and the systemic tests with the spider mite and the eurygaster. Results of tests are set forth in Table 2.

The majority of the tested compounds had low activity as systemic acaricides. Only a few preparations, such as P-250, P-251 and P-254, possess a certain transient systemic activity.

EXPERIMENTAL

Diethyl (carbomethoxy-2-propenyl)phosphate (P-251). To a cooled mixture of 11.6 g of methyl acetoacetate and 10.5 g of triethylamine was added 17.2 g of diethyl chlorophosphate followed by 100 ml of dry ether. The mixture was stood overnight. The precipitated triethylamine hydrochloride was filtered off and washed with ether; the ether was distilled off and the residue distilled in vacuo. Redistillation gave 18.2 g (72.7%).

Diethyl (2-pentenonyl)phosphate (P-252). Prepared as above from 10 g of acetylacetone, 10.5 g of triethylamine and 17.2 g of diethyl chlorophosphate. Redistillation gave 8.4 g (35%).

Dimethylaminoethyl (carbomethoxy-2-propenyl)phosphate (P-255). To a benzene solution of 8.7 g of α-chloromethylacetoacetate was added at 16-18° a benzene solution of 9.6 g of dimethylamidodiethyl phosphite [9]. After heating for 2 hr at 70-80°, the benzene was distilled off and the residue distilled in vacuo. Redistillation gave 3.2 g (22%).

TABLE 2. Relative Toxicity of Derivatives of β-Ketoalkenyl Compounds for Mealy Bugs in Contact Tests

Laboratory numbers	LK-95-100	Laboratory numbers	LK-95-100
P-249	0.4	P-255	0.075
P-250	0.2	P-257	0.1
P-251	0.01	P-259	0.075
P-252	0.2	P-263	0.05–0.075
P-253	0.15	P-264	0.15
P-254	0.025	Parathion	0.03

Dimethylamidodiethyl (2-pentenonyl)phosphate (P-264). To a benzene solution of 16.5 g of dimethylamidodiethyl phosphite was added at 10-15° a benzene solution of 13.5 g of α-chloroacetylacetone. After an hour at 70°, the benzene was distilled off and the residue distilled in vacuo. The third distillation gave 5.1 g (21.7%).

Diethyl (carbomethoxy-2-propenyl)phosphate (P-248). To an ethereal solution of 16.1 g of methyl acetoacetate and 15 g of triethylamine was added at 20° an ethereal solution of 21.4 g of diethyl chlorophosphite. The precipitated triethylamine hydrochloride was filtered off, the ethereal solution dried with sodium sulfate, the ether distilled off, and the residue distilled in vacuo. Redistillation gave 18.8 g (58.2%).

Diethyl (2-pentenonyl)phosphite (P-178). Acetylacetone (7.9 g), diethyl chlorophosphite (12.2 g) and triethylamine (8 g) were reacted by the preceding method. Redistillation gave 6.4 g (37.3%).

Dimethylamidoethyl (carbomethoxy-2-propenyl)phosphite (P-256). Similarly prepared from 11.6 g of methyl acetoacetate, 10.2 g of triethylamine and 15.6 g of dimethylamidoethyl chlorophosphite (b.p. 52-56° at 13.5 mm, d_4^{20} 1.0802, n_D^{20} 1.4678). Redistillation gave 15.2 g (51.9%).

Dimethylamidoethyl(2-pentenonyl)phosphite (P-249). Similarly prepared from 15 g of acetylacetone, 15.8 g of triethylamine and 23.3 g of dimethylamidoethylchlorophosphite. Redistillation gave 18.3 g (55.8%).

Tetramethyldiamido(carbomethoxy-2-propenyl)phosphite (P-258). Similarly prepared from 16.4 g of methyl acetoacetate, 15.2 g of triethylamine and 20 g of tetramethyl diamidochlorophosphite (b.p. 64-65° at 11 mm, d_4^{20} 1.0760, n_D^{20} 1.5045). Redistillation gave 10.6 g (32%).

Diethyl(carbomethoxy-2-propenyl)thiophosphate (P-254). Diethyl (carbomethoxy-2-propenyl)phosphite (17.6 g) and sulfur (2.5 g) in carbon disulfide (15 ml) were heated for 7 hr at 50-55°. The solvent was distilled off and the residue distilled in vacuo. Redistillation gave 15 g (75%).

Diethyl (2-pentenonyl)thiophosphate (P-250). Similarly prepared from 10 g of diethyl (2-pentenonyl)phosphite, 1.6 g of sulfur in 15 ml of carbon disulfide with heating for 5 hr at 55-60°. Yield 3.5 g (28.3%).

Dimethylamidoethyl (carbomethoxy-2-propenyl)thiophosphate (P-257). Prepared similarly from 9.7 g of dimethylamidoethyl (carbomethoxy-2-propenyl)phosphite in 8 ml of carbon disulfide and 1.33 g of sulfur with heating for an hour at 50°. Yield 7.3 g (66.2%.

Dimethylamidoethyl (2-pentenonyl)thiophosphate (P-253). Prepared from 8.6 g of dimethylamidoethyl (2-pentenonyl)phosphite in 8 ml of carbon disulfide and 1.3 g of sulfur. The reaction was violent; subsequently the mixture was heated for 30 min at 50°. Yield 4.1 g (41.6%).

Tetramethyldiamido(carbomethoxy-2-propenyl)thiophosphate (P-259). Prepared from 10 g of tetramethyldiamido(carbomethoxy-2-propenyl)phosphite, 1.4 g of sulfur in 10 ml of carbon disulfide with heating at 50-55° for 3 hr. Yield 4.7 g (42%).

Diethyl (carbomethoxydichloro-2-propyl)phosphate (P-263). A stream of dry chlorine was passed through a solution of 10.8 g of diethyl(carbomethoxy-2-propenyl)phosphate in 18 ml of carbon tetrachloride until the weight had increased by the theoretical amount. After standing for 2 hr at room temperature, the solvent was taken off in vacuo. Redistillation gave 9.7 g (70.1%).

SUMMARY

1. Derivatives of diethyl-, dimethylamidoethyl- and tetramethyldiamidophosphorous acids and of the enol forms of acetylacetone and methyl acetoacetate were synthesized.

2. A series of derivatives of diethyl-, dimethylamidoethyl- and tetramethyldiamidophosphoric and -thiophosphoric acids, containing residues of the enol forms of acetylacetone or methyl acetoacetate, were synthesized.

3. The synthesized compounds were examined in the laboratory for their value as contact and systemic insecticides. Compounds with a carbomethoxypropenyl group were stronger contact poisons for mealy bugs than compounds containing the pentenonyl group. A high contact toxicity, surpassing that of Parathion, is exhibited by compound P-251. Compound P-254 is slightly more toxic than Parathion.

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TRIS(TRIORGANOSILYL) PHOSPHATES

N. F. Orlov and M. G. Voronkov

Institute of Silicate Chemistry, Academy of Sciences of the USSR
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2223-2229, July, 1960
Original article submitted July 11, 1959

Monomeric and polymeric organosilicon derivatives of acids of phosphorus have attracted the attention of many investigators in recent years [1-17].

In the present work we describe new routes for synthesis of tris(triorganosilyl) phosphates starting from thioorganosilanols, hexaorganodisiloxanes or triorganosilanes.

We found that tris(triorganosilyl) phosphates are formed in 50% yield by reaction of phosphorus pentoxide with triorganosilanols according to the equation*

$$12R_3SiOH + P_4O_{10} \longrightarrow 4(R_3SiO)_3PO + 6H_2O. \quad (1)$$

Due to the relatively great susceptibility of triorganosilanols to intermolecular anhydrocondensation with formation of hexaalkyldisiloxanes, which is catalyzed in particular by phosphorus pentoxide [18], we cannot exclude the possibility of reaction (1) being accompanied by reaction (2), already described by one of us [2]**

$$6R_3SiOSiR_3 + P_4O_{10} \longrightarrow 4(R_3SiO)_3PO. \quad (2)$$

The mechanism of reaction of triorganosilanols with phosphorus pentoxide may be represented by the following equations:

$$\left(-O-\overset{\overset{O}{\|}}{\underset{|}{P}}-O-\right)_3P{=}O + HOSiR_3 \rightleftarrows \left(-O-\overset{\overset{O}{\|}}{\underset{|}{P}}-O-\right)_3P{=}O\cdots H\cdots OSiR_3 \rightleftarrows$$

$$\rightleftarrows \left(-O-\overset{\overset{O}{\|}}{\underset{|}{P}}-O-\right)_3\overset{+}{P}OH + {}^{-}OSiR_3 \rightleftarrows \left(-O-\overset{\overset{O}{\|}}{\underset{|}{P}}-O-\right)_2P\overset{OH}{\underset{O}{\diagdown\!\!\diagup}} + R_3SiO-\overset{\overset{O}{\|}}{\underset{|}{P}}-O-;$$

$$\left(-O-\overset{\overset{O}{\|}}{\underset{|}{P}}-O-\right)_2P\overset{OH}{\underset{O}{\diagdown\!\!\diagup}} + HOSiR_3 \rightleftarrows \left(-O-\overset{\overset{O}{\|}}{\underset{|}{P}}-O-\right)_2P\overset{OSiR_3}{\underset{O}{\diagdown\!\!\diagup}} + H_2O \quad (3)$$

and so on until the whole of the cyclic structure of P_4O_{10} has been broken down to monomeric molecules of $(R_3SiO)_3PO$.

Another method that we developed for synthesis of tris(triorganosilyl) phosphates (yields up to 90%) is based on reaction of triorganosilanols with orthophosphoric acid:

* We previously utilized a similar reaction for synthesis of triorganosiloxy derivatives of boron [19], vanadium [20] and antimony [21].

** It is interesting to note that phosphorus pentoxide does not react on boiling with hexachlorodisiloxane, due to the oxygen atom of $Cl_3SiOSiCl_3$ being devoid of nucleophilic properties.

$$3R_3SiOH + H_3PO_4 \rightleftarrows (R_3SiO)_3PO + 3H_2O. \quad (4)$$

Unlike the formation of bis(trialkylsilyl) sulfates, which takes place only on direct interaction between triorganosilanols and sulfuric acid [22], reaction (4) took place under conditions of azeotropic distillation of the water formed in the reaction mixture.*

Reaction between triorganosilanols and orthophosphoric acid may be represented by the following mechanism:

$$R_3SiOH + H_3PO_4 \rightleftarrows R_3SiOH_2^+ + \begin{matrix} HO \\ HO \end{matrix}\!\!>\!\!P(=O)\!-\!O^- \rightleftarrows R_3SiO\!-\!P(=O)(OH)_2 + H_2O;$$

$$R_3SiO\!-\!P(=O)(OH)_2 + R_3SiOH \rightleftarrows R_3SiOH_2^+ + R_3SiO\!-\!P(=O)(OH)\!-\!O^- \rightleftarrows \quad (5)$$

$$\rightleftarrows (R_3SiO)_2P(=O)\!-\!OH + H_2O; \quad \text{etc.}$$

The first reaction step is transfer by phosphoric acid of a proton to the silanol with formation of a siloxonium ion (B). Subsequent nucleophilic action of anion (A) on (B) leads to release of a molecule of water and formation of the substitution product (C):

$$\underset{(A)}{(HO)_2P(=O)\!-\!O^{(-)}} \longrightarrow \underset{(B)}{SiR_3\!-\!OH_2^{(+)}} \rightleftarrows \underset{(C)}{(HO)_2P(=O)\!-\!O\!-\!SiR_3} + H_2O. \quad (6)$$

The two succeeding reaction steps may be visualized in similar fashion. Reaction of triorganosilanols with other acids also proceeds by the same mechanism.

It is interesting to note that a similar reaction of organic alcohols with orthophosphoric acid only leads to formation of a mixture of acid esters of phosphoric acids [26]. This can be explained in terms of the large steric hindrances arising during nucleophilic attack of the carbon atom (1.5 times smaller than the silicon atom) by $(RO)HOP(=O)\text{-}O^-$ anions and in particular by $(RO)_2P(=O)\text{-}O^-$ anions. To this we must add that silicon, due to the presence of vacant 3rd orbitals, enters very much more easily than carbon into reactions of the SN2 type with nucleophilic reagents.

We were unsuccessful in our attempt to synthesize tris(triethylsilyl) phosphate by reaction of triethylsilanol with phosphorus oxychloride in presence of pyridine in accordance with the equation**

$$3(C_2H_5)_3SiOH + 3C_5H_5N + POCl_3 \longrightarrow [(C_2H_5)_3SiO]_3PO + 3C_5H_5N \cdot HCl. \quad (7)$$

The whole of the triethylsilanol was recovered unchanged, and the phosphorus oxychloride formed a solid complex with pyridine of the composition $3C_5H_5N \cdot POCl_3$.*** The rate of reaction of phosphorus oxychloride with pyridine is evidently very much greater than the speed of reaction (7).

We were able to react orthophosphoric acid with hexaalkyldisiloxanes in accordance with the equation

$$3R_3SiOSiR_3 + 2H_3PO_4 \overset{H^+}{\rightleftarrows} 2(R_3SiO)_3PO + 3H_2O. \quad (8)$$

Hexaalkyldisiloxanes are known to easily form bis(trialkylsilyl) sulfates with sulfuric acid [22,23]. Phosphoric acid, however, practically does not react with hexaalkyldisiloxanes under similar conditions. Hurd showed [24] that

*We may point out that triorganosilanols can only react with weak organic acids in presence of electrophilic catalysts (zinc chloride, sulfuric acid).

**The analogous reaction of $VOCl_3$ with triorganosilanols leads to formation of tris(triorganosilyl) vanadates [20].

***It is interesting that $(CH_3)_3SiOP(O)Cl_2$ also reacts anomalously with alcohol in presence of pyridine with formation of $(CH_3)_3SiOC_2H_5$ [14].

85% (sirupy) orthophosphoric acid also differs from sulfuric acid in not causing rearrangement of siloxanes either at ordinary or at elevated temperature. Nevertheless, if the water of reaction is at once withdrawn (especially in presence of H_2SO_4 or $ZnCl_2$ as catalyst), hexaalkyldichlorosiloxanes smoothly react with orthophosphoric acid according to equation (8).

We propose the following mechanism of reaction of hexaalkyldisiloxanes with orthophosphoric acid in presence of sulfuric acid:

$$R_3SiOSiR_3 + H^+ \rightleftarrows R_3Si-\overset{+}{\underset{|}{O}}\underset{H}{}-SiR_3;$$

$$R_3Si\overset{+}{O}SiR_3 + (HO)_3P{=}O \rightleftarrows R_3Si\overset{+}{O}H_2 + R_3SiOP\begin{matrix}O\\ \diagup\\ \diagdown\\ (OH)_2\end{matrix}; \qquad (9)$$

$$R_3Si\overset{+}{O}H_2 \rightleftarrows R_3SiOH + H^+ \quad \text{etc.}$$

Concerning the action of zinc chloride, the latter functioning as an ansolvo acid evidently forms a strong complex acid

$$H^+[(HO)_2\overset{O}{\overset{\|}{P}}-O \rightarrow ZnCl_2]^-,$$

with orthophosphoric acid which is also a catalyst for the reaction.

A new and interesting route to tris(trialkylsilyl) phosphates was found in the reaction of triorganosilanes with orthophosphoric acid in presence of colloidal nickel as catalyst.

$$3R_3SiH + (HO)_3PO \xrightarrow{Ni} (R_3SiO)_3PO + 3H_2. \qquad (10)$$

This reaction differs from that of triorganosilanes with boric acid [15] in that it is accompanied by formation of hexaorganodisiloxanes in a secondary reaction possibly due to interaction of trialkylsilanols with the water present in the orthophosphoric acid and formed during its dehydration [25].

$$2R_3SiH + HOH \xrightarrow{Ni} R_3SiOSiR_3 + H_2. \qquad (11)$$

Because of this secondary reaction, the yield of tris(triorganosilyl) phosphates does not exceed 60%.

In our opinion, the mechanism of the nickel-catalyzed reaction of trialkylsilanes with acids of phosphorus and with other substances containing OH groups is based on retention by the positively charged surface of nickel of hydride hydrogen bound to silicon with formation of a surface compound:

$$R_3SiH + Ni \longrightarrow R_3Si \cdots H \cdots Ni.$$

The reaction is apparently completed by nucleophilic attack of the chemisorbed molecule by the hydroxyl-containing molecule followed by recombination and dissociation.

$$\begin{matrix}R_3Si \cdots H \cdots Ni\\ \uparrow\\ R'-O-H\end{matrix} \longrightarrow \begin{matrix}R_3Si\\ |\\ R'-O\end{matrix} + H_2 + Ni.$$

We cannot submit accurate kinetic evidence in support of this mechanism. It is consistent, however, with the already established marked dependence of the reaction rate on the quantity of catalyst.

All of the tris(triorganosilyl) phosphates that we prepared are stable in dry air; they are decomposed, however, by moist air with cleavage of the SiOP bond. Their properties are set forth in the table.

Tris (triorganosilyl) Phosphates

$(R_3SiO)_3PO$	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	Yield (%)	% Si		% P		Obtained by reaction
					calculated	found	calculated	found	
$[(CH_3)_3SiO]_3PO$	110—112° (10)	0.9602	1.4080	60.0	26.79	—	9.85	10.10, 10.06	8***
	161—163 (80)	—	1.4075	25.0	26.79	—	9.85	9.68, 9.53	8**
$[(CH_3)_2C_2H_5SiO]_3PO$*	117—121 (3)	0.9632	1.4223	45.0	23.63	—	8.69	8.18, 8.33	8***
	180—181 (35)	0.9663	1.4465	80.0	19.12	19.10, 19.34	7.03	6.70, 6.47	4
$[(C_2H_5)_3SiO]_3PO$	178—181 (4)	0.9663	1.4452	51.0	19.12	19.35, 18.70	7.03	6.59, 6.42	8**
	202—205 (10)	0.9668	1.4445	51.0	19.12	19.18, 18.87	7.03	7.00, 7.01	1
	182 (4)	0.9675	1.4429	57.5	19.12	19.08, 18.86	7.03	6.87, 6.72	10
$[(C_6H_5)_3SiO]_3PO$*	M.p. 244°	—	—	85.0	9.65	9.67, 9.65	3.55	3.52, 3.77	4

* New compound.
** Sulfuric acid as catalyst.
*** Zinc chloride as catalyst.

EXPERIMENTAL

Starting components. Crystalline orthophosphoric acid and phosphorus pentoxide ("chem. pure grades") were used without supplementary purification. Triethylsilanol was prepared by hydrolysis of triethylchlorosilane with 1 N sodium hydroxide solution in presence of phenolphthalein as indicator. Triphenylsilanol was synthesized by treatment of triphenylethoxysilane with acetic acid in presence of a few drops of sulfuric acid and was purified by two recrystallizations from benzene. Hexaalkyldisiloxanes were prepared by hydrolysis of the corresponding trialkylhalosilanes. Triethylsilane was synthesized by reaction of ethylmagnesium bromide with ethyldichlorosilane. All starting organosilicon compounds were purified by distillation through a column and possessed constants agreeing with those in the literature.

Analysis. Silicon was determined in the organosilicon compounds by treatment of a weighed sample with a mixture of oleum and nitric acid, filtration of the precipitated silicic acid and calcination at 900°. Phosphorus was determined in the filtrate by precipitation with magnesium chloride after treatment of the filtrate with aqueous ammonia.

Procedure for synthesis. All reactions involving formation of water were carried out in an all-glass apparatus comprising a round-bottomed flask connected to a water trap with a tap and to a reflux condenser. Water was removed from the reaction mixture by continuous azeotropic distillation with an inert solvent (benzene, toluene) and was collected in the trap.

Tris (triethylsilyl) phosphate from triethylsilanol and phosphoric acid (reaction 1). A mixture of 3.2 g (0.02 mole) of phosphorus pentoxide, 16 g (0.12 mole) of triethylsilanol and 100 ml of benzene was boiled for 4 hr until water ceased to come off and the phosphorus pentoxide had dissolved completely. The benzene was distilled off and the residue fractionated in vacuo. There was obtained 9 g (51%) of tris (triethylsilyl) phosphate with b.p. 202-205° (10 mm); n_D^{20} 1.4445.

Tris (triethylsilyl) phosphate from triethylsilanol and orthophosphoric acid (reaction 4). A mixture of 16 g (0.12 mole) of triethylsilanol, 4 g (0.4 mole) of orthophosphoric acid and 80 ml of benzene was boiled for 6 hr, during which period 2.6 ml of water was distilled off. Fractionation of the reaction mixture (after distillation of the benzene) gave 16 g (90.9%) of tris (triethylsilyl) phosphate with b.p. 175-181° (3 mm). After redistillation the compound had the constants given in the table.

Tris (triphenylsilyl) phosphate from triphenylsilanol and orthophosphoric acid (reaction 4). Heating of a mixture of 16.6 g (0.06 mole) of triphenylsilanol, 1.96 g (0.02 mole) of orthophosphoric acid and 100 ml of toluene for 8 hr led to separation of about 1 ml of water. The resulting finely crystalline precipitate of tris (triphenylsilyl) phosphate was twice recrystallized from benzene and had m.p. 244°. Poorly soluble in acetone, hexane and ethyl acetate; readily soluble in butyl alcohol, toluene and dioxane.

Tris(triethylsilyl) phosphate from phosphorus oxychloride and triethylsilanol in presence of pyridine (reaction 7). To a solution of 16 g (0.12 mole) of triethylsilanol and 8.7 ml (0.11 mole) of pyridine in 120 ml of benzene, cooled to -3°, was slowly added a solution of 6.1 g (0.04 mole) of phosphorus oxychloride in 30 ml of benzene at such a rate that the temperature of the mixture did not rise above +5°. A precipitate at once began to come down. After the whole of the phosphorus oxychloride had been added, the mixture was heated for 2 hr at 70-80°. The cooled reaction mixture was filtered, and the precipitate was washed with dry benzene and analyzed for its phosphorus content.

Found %: P 7.80, 7.37. $POCl_3 \cdot 3C_5H_5N$. Calculated %: P 7.95.

After distillation of the benzene the filtrate was distilled in vacuo to give 12 g of unchanged triethylsilanol and a small quantity of the product of its anhydridization—hexaethyldisiloxane. A repeat experiment gave similar results.

Tris(trimethylsilyl) phosphate from hexamethyldisiloxane and orthophosphoric acid (reaction 8). a) mixture of 19.5 g (0.12 mole) of hexamethyldisiloxane, 7.95 g (0.08 mole) of orthophosphoric acid, 100 ml of benzene and three drops of sulfuric acid was boiled for 8 hr, during which period 2.2 ml of water came off. After the benzene had been distilled off, the residue was fractionated in vacuo to give 6 g (25%) of tris(trimethylsilyl) phosphate with b.p. 161-163° (80 mm); n_D^{20} 1.4075.

b) A mixture of 39 g (0.24 mole) of hexamethyldisiloxane, 15.7 g (0.16 mole) of orthophosphoric acid, 1 g of zinc chloride and 100 ml of benzene was heated under similar conditions for 12 hr and gave 4.4 ml of water. Distillation of the residue gave 30 g (60%) of tris(trimethylsilyl) phosphate with b.p. 110-112° (10 mm); n_D^{20} 1.4080.

$[(CH_3)_2C_2H_5SiO]_3PO$ and $[(C_2H_5)_3SiO]_3PO$ were similarly prepared in yields of 45 and 51% respectively.

Tris(triethylsilyl) phosphate from triethylsilane and orthophosphoric acid (reaction 10). A mixture of 58 g (0.5 mole) of triethylsilane and 0.5 g of nickel chloride was refluxed until a black precipitate of colloidal nickel had formed. The reaction mixture was cooled and 15.7 g (0.16 mole) of orthophosphoric acid was added. Hydrogen came off when the mixture was heated and the total volume evolved after 4 hr from the start of heating was 8 liters (73%). The temperature of the mixture rose to 207°. Fractional distillation gave 21 g of hexaethyldisiloxane $(C_2H_5)_3SiOSi(C_2H_5)_3$ with b.p. 100° (4 mm); n_D^{20} 1.4330, and 30 g (54.5%) of tris(triethylsilyl) phosphate with b.p. 182° (4 mm); n_D^{20} 1.4429.

SUMMARY

Four new methods of synthesis of tris(triorganosilyl) phosphates were developed, based on reactions of trialkylsilanols with phosphorus pentoxide or phosphoric acid, on catalytic scission of hexaalkyldisiloxanes by phosphoric acid in presence of protonic and aprotonic acids, and on reaction of trialkylsilanes with phosphoric acid in presence of colloidal nickel. These methods were employed for preparation of four tris(triorganosilyl) phosphates, two of which were previously unknown.

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INVESTIGATIONS OF HYDROXY DERIVATIVES OF PHENANTHRENE

I. 1-NITROSO-2-PHENANTHROL AND ITS BISULFITE COMPOUND

S. V. Bogdanov and L. S. Shibryaeva

K. E. Voroshilov Scientific Research Institute for Organic Intermediates and Dyes

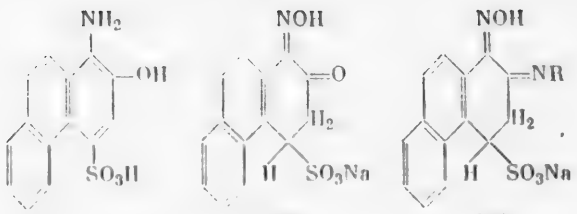
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2229-2235, July, 1960
Original article submitted July 26, 1959

The nitrosation of 2-phenanthrol was studied with the aim of throwing light on the ability of nitroso derivatives of hydroxyphenanthrenes to form compounds similar to those previously obtained from 1-nitroso-2-naphthol [1] and from 1-nitroso-2-anthrol [2]. Some properties of the reaction product were investigated.

The experiments showed that nitrosation of 2-phenanthrol by a mixture of sodium nitrite and zinc chloride or aluminum sulfate in an alcoholic medium, also by nitrous acid in an aqueous medium, proceeds rather sluggishly. The product of nitrosation resembled 1-nitroso-2-naphthol and 1-nitroso-2-anthrol in forming a soluble bisulfite compound with sodium bisulfite. The latter is quantitatively decomposed by alkalies to a salt of nitrosophenanthrol and sulfite. This facilitated the separation of the nitrosophenanthrol from the crude nitrosation product. Reduction of the nitroso compound by stannous chloride led to 1-amino-2-phenanthrol, which was identical with the product of cleavage of the azo compound of 2-phenanthrol [3]. It follows therefore that the nitroso compound has the structure of 1-nitroso-2-phenanthrol.

The bisulfite compound prepared from 1-nitroso-2-phenanthrol has the composition $C_{14}H_8(NO)(OH)\cdot NaHSO_3\cdot 0.5H_2O$. It is stable in the solid state and in neutral or weakly acid solutions at the ordinary temperature. Reduction of the bisulfite compound by excess of bisulfite at the boil or by stannous chloride in hydrochloric acid leads to 1-amino-2-phenanthrol and 1,2-dihydroxyphenanthrene, whereas reduction with sulfurous acid in presence of hydrochloric acid leads to isolation of only 1,2-dihydroxyphenanthrene. The structure of (I) was established by oxidation with nitric acid to 1,2-phenanthrenequinone-4-sulfonic acid and by conversion of the latter with p-toluidine [3] into the p-toluidine salt of 1,2-dihydroxyphenanthrene-4-sulfonic acid which was identical with the compound obtained directly from 1,2-dihydroxyphenanthrene-4-sulfonic acid [3]. Formation of (I) on reduction of the bisulfite compound with stannous chloride is analogous to the conversion of the bisulfite compounds of 1-nitroso-2-naphthol and 1-nitroso-2-anthrol under similar conditions into, respectively, 1-amino-2-naphthol-4-sulfonic acid [1] and 1-amino-2-anthrol-4-sulfonic acid [2], but in lower yield.

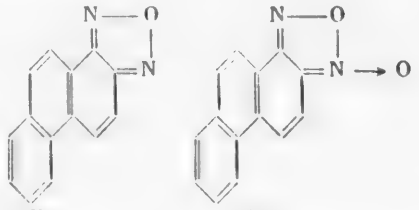
Treatment of the bisulfite compound of nitrosophenanthrol with hydroxylamine, semicarbazide and phenylhydrazine in an acetic acid medium gave respectively the oxime, semicarbazone and phenylhydrazone of the bisulfite compound. The ability of the bisulfite compound to react with hydroxylamine and similar compounds and its transformation into (I) on reduction show that a free keto group is present and that the sulfonic group is in the 4-position. On this basis we can picture the bisulfite compound of 1-nitroso-2-phenanthrol as 3,4-dihydro-1,2-phenanthrenequinone-1-oxime-4-sulfonic acid (II), and we can represent the structure of its oxime, semicarbazone and phenylhydrazone by formulas (IIIa, b, c).



(I) (II) (III)

(IIIa) R = OH,
(IIIb) R = NHCONH$_2$,
(IIIc) R = NHC$_6$H$_5$.

Short-period treatment of compound (IIIa) with sodium hydroxide leads to removal of sulfurous acid and to formation of 1,2-phenanthrenequinonedioxime; longer treatment with alkali gives 1,2-phenanthrofurazan (IV); oxidation of 1,2-phenanthrenequinonedioxime with dilute nitric acid leads to 1,2-phenanthrofuroxan (V); the position of the isolated oxygen atom was not established.



(IV) (V)

Conversions of (II) into (IIIa) and of the latter into 1,2-phenanthrenequinonedioxime and then into (IV) or (V) are analogous to the transformations of the corresponding derivatives of 1-nitroso-2-naphthol and 1-nitroso-2--anthrol.

EXPERIMENTAL

1-Nitroso-2-phenanthrol. 1) To a solution of 8.6 g (0.04 mole) of 90.2% 2-phenanthrol in a mixture of 8.66 g of 20.7% solution of sodium hydroxide, 0.5 g of sulfite lye and 960 ml of water at 2-4° in the course of 15 min was added 10.9 g of 17.4% hydrochloric acid. To the resulting suspension was added 6.07 g of sodium nitrite, and in the course of 2-2.5 hr at 2-4° 21 g of 17.4% hydrochloric acid was run in. After being stirred for 3-4 hr, the mass was stood overnight. The brownish-red precipitate was filtered and washed with water. Into a suspension of the precipitate in 80 ml of water were run 14 g (0.05 mole) of 37.2% sodium bisulfite solution and 0.75 ml of pyridine, and the suspension was stirred for 48 hr at 20-22° until the red color had disappeared. The insoluble residue was filtered (4.42 g containing 58.2% of 2-phenanthrol). To the filtrate was added 28.7 g of 20.7% sodium hydroxide solution; the suspension of the precipitated yellow sodium salt of 1-nitroso-2-phenanthrol was stirred for 20 min and poured into 130 ml of 6% hydrochloric acid. The red precipitate of 1-nitroso-2-phenanthrol was filtered. Yield 4.0 g (44.7% calculated on the phenanthrol taken). M.p. 175.6-176.4° (decomp.). After prolonged standing, the filtrate from the 1-nitroso-2-phenanthrol deposited 0.5 g of 1,2-dihydroxyphenanthrene. Needles (from dilute hydrochloric acid) with m.p. 175.3-176°.

2) To a solution of 1.02 g of 99.8% 2-phenanthrol in 10 ml of alcohol at 30° was added a solution of 0.72 g of 98% zinc chloride in 1 ml of water, followed in the course of 1.5 hr by a solution of 0.8 g of sodium nitrite in 1.5 ml of water. The mixture was boiled for 2.5 hr. The red-brown precipitate was filtered and washed with alcohol (unchanged phenanthrol was found in the aqueous alcoholic filtrate). The precipitate was stirred with dilute hydrochloric acid, and the impure nitrosophenanthrol was filtered and washed with water; yield 0.45 g, m.p. 174-176° (decomp.).

3) To a solution of 1.02 g of 99.8% phenanthrol in 15 ml of alcohol was added a solution of 1.2 g of crystalline aluminum sulfate in 1.5 ml of water and in the course of 1 hr a solution of 0.69 g of sodium nitrite in 2.5 ml of water. The mixture was held at 20-22° for 18 hr. The brown precipitate was filtered, washed with water, with dilute hydrochloric acid and again with water and alcohol; weight of precipitate 0.3 g; m.p. 132-136°. Dilution of the alcoholic filtrate with half its volume of water led to separation of an additional 0.56 g of solid with m.p. 118-122°. Treatment of both precipitates with bisulfite and decomposition of the bisulfite compound yielded 0.35 g of nitrosophenanthrol with m.p. 175-176°. The bisulfite-insoluble residue was impure phenanthrol.

1-Nitroso-2-phenanthrol forms red needles (from alcohol or acetic acid), insoluble in water, sparingly soluble in cold alcohol and acetic acid. M.p. 181.4-181.5° (decomp.). A yellow-green precipitate comes down when iron sulfate is added to the alcoholic solution acidified with acetic acid.

Found %: C 75.40, 75.38; H 4.26, 4.24; N 6.33, 6.31. $C_{14}H_9O_2N$. Calculated %: C 75.32; H 4.06; N 6.27.

1-Amino-2-phenanthrol. To a solution of 1.13 g of 1-nitroso-2-phenanthrol (m.p. 181°) in 50 ml of alcohol was added 10 ml of 38.5% solution of stannous chloride in concentrated hydrochloric acid, and the mixture boiled for an hour. The aminophenanthrol hydrochloride was filtered, washed with dilute hydrochloric acid and reprecipitated from alcohol by hydrochloric acid. Yield 1.12 g; fine, colorless needles.

Diacetyl compound: fine, colorless needles, m.p. 224.8-225.2°. 1-Amino-2-phenanthrol was prepared for comparison by reduction of the azo dye from 2-phenanthrol and sulfanilic acid with sodium hydrosulfite [3]. M.p. 224.5 225°. Mixture of specimens of the diacetyl compounds had m.p. 224.8-225.6°.

Bisulfite compound of 1-nitroso-2-phenanthrol (II). To a suspension of 6.69 g (0.03 mole) of 1-nitroso-2-phenanthrol (m.p. 181-181.3°) in 60 ml of water were added 0.6 ml of pyridine and 16.77 g (0.06 mole) of 37.2% sodium bisulfite solution. The suspension was stirred at 18-20° for 28 hr (in the absence of pyridine for 32 hr). To the solution was added sodium chloride (20% by volume), and the precipitate was filtered 20 hr later and washed with sodium chloride solution, alcohol and ether; yield of 87.6% substance 7.82 g (69.82%). The filtrate was made alkaline with sodium hydroxide and acidified with hydrochloric acid; 1.1 g of nitrosophenanthrol came down with m.p. 176-177°. After prolonged standing, the acid filtrate deposited 0.53 g of 1,2-dihydroxyphenanthrene with m.p. 171.3-173° (diacetyl derivative with m.p. 145-146°; a mixture with the diacetyl derivative obtained via 1,2-phenanthrenequinone [3] melts at 145.6-146.4°).

The bisulfite compound crystallized from 90% alcohol. The sodium salt was fairly easily soluble in water, sparingly in alcohol; at the ordinary temperature the aqueous solutions are yellow but they turn brown when heated. A yellowish-green precipitate comes down when the aqueous solution is treated with ferrous sulfate and sodium carbonate.

Long, colorless, rectangular plates; contain 0.5 mole of water which is not removed at 100-110°; decomposes at 115-120°.

For analysis of the bisulfite compound, a 0.4-0.5 sample was dissolved in 50 ml of water, 5 ml of 40% sodium hydroxide solution was added, followed after 10 min by 1500 ml of distilled water. The solution was acidified with 10 ml of 34.4% hydrochloric acid and the orange-red suspension titrated with 0.1 N iodine solution.

Found %: C 49.73, 50.02; H 3.45; 3.20; N 4.15, 4.09; S 9.61, 9.46. M 337.7 (iodometrically). $C_{14}H_{10}O_5NSNA \cdot 0.5\,H_2O$. Calculated %: C 50.00; H 3.29; N 4.16; S 9.52. M 336.3.

Reduction of (II). a) With sulfurous acid. The crude product of nitrosation of 0.04 mole of 90.2% phenanthrol was treated as described above with 0.08 mole of bisulfite in presence of pyridine. Into the bisulfite solution was run 10 ml of 35.4% hydrochloric acid and the well-stoppered mixture stood for 7 days at 20°. The precipitated 1,2-dihydroxyphenanthrene was filtered and washed with water; yield 3.32 g with m.p. 158-160.4°; fine, colorless needles (from dilute hydrochloric acid), m.p. 174.8-175.6°. Diacetyl derivative: fine, colorless needles (from aqueous alcohol), m.p. 146.4-147.2°. A mixture with the diacetyl derivative prepared via 1,2-phenanthrenequinone [3] melted at 146.2-146.6°.

b) With sodium bisulfite. A solution of 5.6 g of 87.64% preparation (II) and 8.1 g of 37.2% bisulfite solution in 150 ml of water was boiled for 2 hr until (II) disappeared. After the solution had been acidified with 6 ml of 35.4% hydrochloric acid, 3.48 g of reaction product came down in the course of 5 days. The precipitate was separated into its components by heating at 50-60° with a solution of 4.14 g of 37.2% sodium bisulfite solution and 2.04 g of crystalline sodium carbonate in 100 ml of water; the insoluble residue was filtered. Treatment of the filtrate with hydrochloric acid brought down 0.88 g of (I). Fractional crystallization of the residue from dilute hydrochloric acid yielded 0.82 g of 1-amino-2-phenanthrol (diacetyl derivative: m.p. 225.2-226°) and 0.4 g of 1,2-dihydroxyphenanthrene (diacetyl derivative: m.p. 146.2-147°).

c) With stannous chloride. To a solution of 1.87 g of 87.64% preparation (II) in 100 ml of water was added a solution of 2.4 g of stannous chloride in 5 ml of 35.4% hydrochloric acid, and the mixture was stood for 6 days at 18-20°. The precipitate was filtered and washed with water and alcohol; weight 1.1 g. Treatment for separation of

the reaction products gave 0.32 g of (I) and 0.54 g of a mixture of 1-amino-2-phenanthrol (diacetyl derivative: m.p. 225-226°) and 1,2-dihydroxyphenanthrene (m.p. 174-175°, diacetyl derivative with m.p. 146.2-146.8°).

1-Amino-2-phenanthrol-4-sulfonic acid (I): pale grayish, small needles, insoluble in water and alcohol. With nitrite in presence of copper sulfate it forms a brown solution from which sodium chloride brings down yellow needles of diazo compound. The diazo compound is readily soluble in water and sparingly in alcohol; with resorcinol in a sodium carbonate medium it forms blue-violet crystals; with 2-naphthol-3,6-disulfonic acid it does not give a coupling product.

Found %: H_2O 5.78 (dried at 105-110°); C 54.85, 54.75; H 4.32, 4.5; N 4.47, 4.39; S 10.30. $C_{14}H_{11}O_4NS \cdot H_2O$. Calculated %: H_2O 5.86; C 54.71; H 4.26; N 4.56; S 10.43.

p-Toluidine salt of 1,2-dihydroxyphenanthrene-4-sulfonic acid. A suspension of 0.61 g of (I) in 10 ml of 20.22% nitric acid was stirred for 8 hr at 18-20°. The dark-red solution was filtered and sodium chloride (20% by volume) was introduced into the filtrate. The red precipitate of sodium salt of phenanthrenequinonesulfonic acid was filtered and reprecipitated from aqueous solution with alcohol. Yield 0.35 g; red plates.

To a solution of 0.15 g of the sodium salt in 7 ml of hot water was added 0.05 g of p-toluidine and the mixture stood for an hour. Addition of hydrochloric acid brought down the p-toluidine salt of 1,2-dihydroxyphenanthrene-4-sulfonic acid; yield 0.09 g; yellow plates (from 6-7% hydrochloric acid) with m.p. 245.8-247.3° (decomp.). This salt was prepared for comparison from 1,2-dihydroxyphenanthrene-4-sulfonic acid [3]; m.p. 246-247° (decomp.). A mixed specimen melted at 246-247° (decomp.).

Oxime (IIIa). To a solution of 7.46 g of 87.6% preparation (II) in 120 ml of water was added 3.26 g of crystalline sodium acetate and 1.53 g of hydroxylamine hydrochloride, and the solution was stood for 38 hr at 18-20°. Sodium chloride (20% by volume) was added to the solution, and after 22 hr the sodium salt of (IIIa) was filtered and washed with sodium chloride solution, alcohol and ether; yield 5.95 g (82.63%).

Sodium salt of (IIIa): long, yellowish plates (from alcohol); rather sparingly soluble in water, less soluble in alcohol; gives a brown color with ferric chloride in an aqueous medium.

Found %: H_2O 5.03 (dried at 120-125°); C 46.52, 46.77; H 3.88, 3.95; N 7.69, 7.70; S 8.86. $C_{14}H_{11}O_5N_2SNa \cdot H_2O$. Calculated %: H_2O 4.99; C 46.66; H 3.63; N 7.77; S 8.89.

Semicarbazone (IIIb). To a solution of 1.95 g of 83.6% preparation (II) in 30 ml of water were added a solution of 0.62 g of semicarbazide hydrochloride and 1.5 g of crystalline sodium acetate in 7 ml of water; the mixture was stood for 26 hr; the precipitate was filtered and washed with alcohol and ether. Yield 1.93 g (92%). The semicarbazone was reprecipitated from aqueous solution with alcohol. Yellowish prisms, sparingly soluble in alcohol, more soluble in water.

Found %: C 42.72, 42.68; H 4.12, 4.01; N 13.48, 13.44; S 7.71. $C_{15}H_{13}O_5N_4SNa \times 2H_2O$. Calculated %: C 42.85; H 4.07; N 13.32; S 7.62.

Phenylhydrazone (IIIc). A solution of 1.6 g of phenylhydrazine hydrochloride and 4.08 g of crystalline sodium acetate in 5 ml of water was run into a solution of 3.9 g of 83.6% preparation (II) in 60 ml of water. The mixture was stood for 12 hr. The precipitate was filtered and washed with alcohol and ether. Yield 4.43 g (94.05%). Yellowish, lustrous needles (from alcohol), readily soluble in water and more sparingly in alcohol. The substance contains water of crystallization which partly comes off at 120-130°. The substance breaks down at 140°.

Found %: C 50.96, 50.97; H 4.56, 4.72; N 8.94, 9.03; S 6.60. $C_{20}H_{16}O_4N_3SNa \times 3H_2O$. Calculated %: C 50.94, H 4.70; N 8.91; S 6.78.

1,2-Phenanthrenequinonedioxime. To a solution of 7.2 g of (IIIa) in 170 ml of hot water was added 25 ml of 25.6% sodium hydroxide solution, and the liquid was heated to 70° (a red precipitate came down). The mixture was quickly cooled and run into 200 ml of 6% hydrochloric acid; sulfur dioxide was detected by odor, and a yellow precipitate came down. The latter was filtered, washed with water and dried in the air; yield 4.12 g. The filtrate yielded 0.56 g of (IV) after addition of excess of sodium hydroxide and heating. M.p. 172.2-172.6°.

A solution of 4.12 g of 1,2-phenanthrenequinonedioxime was made up in 250 ml of water with addition of 10 ml of 20% sodium hydroxide solution. The insoluble (IV) was filtered and washed with water (0.33 g with m.p. 168.8-171.6°). On acidification the filtrate deposited 3.68 g of 1,2-phenanthrodioxime [77.3% calculated on

the (IIIa)]. Yellow, rectangular prisms (from aqueous alcohol), insoluble in water, difficultly soluble in alcohol and acetic acid; orange-red solutions in alkalies. M.p. 178-178.2° (decomp.).

Found %: N 11.68, 11.71. $C_{14}H_{10}O_2N_2$. Calculated %: N 11.76.

1,2-Phenanthrofurazan (IV). A solution of 3.6 g of (IIIa) in 160 ml of 5% sodium carbonate solution was boiled for 3 hr. The precipitate was filtered and washed with water; yield 2.15 g (97.7%), m.p. 171-172°. Yellowish needles (from aqueous alcohol) with m.p. 172.6-173°, insoluble in water, soluble in alcohol, less readily in acetic acid.

Found %: C 76.29, 76.41; H 3.60, 3.56; N 12.76, 12.72. $C_{14}H_8ON_2$. Calculated %: C 76.35; H 3.66; N 12.72.

1,2-Phenanthrofuroxan (V). A solution of 2.38 g of 1,2-phenanthrenequinonedioxime in a mixture with 8 ml of 8.40% potassium hydroxide solution and 160 ml of water was run in the course of 25 min into 180 ml of 20.22% nitric acid heated to 65-70°, and the mixture was heated at 90° for 15 min. The precipitate was filtered and washed with water; yield 2.16 g (92.33%). M p. 219.8-220.5°. Yellowish needles (from alcohol) with m.p. 221.5-222°, insoluble in water, sparingly soluble in alcohol and acetic acid.

Found %: C 71.27; H 3.52; N 11.89, 11.72. $C_{14}H_8O_2N_2$. Calculated %: C 71.18; H 3.41; N 11.86.

SUMMARY

1. 1-Nitroso-2-phenanthrol is converted by sodium bisulfite into a bisulfite compound which with hydroxylamine, semicarbazide and phenylhydrazine forms the oxime, semicarbazone and phenylhydrazone of the bisulfite compound.

2. Reduction of the bisulfite compound with stannous chloride gives 1-amino-2-hydroxy-4-sulfonic acid in addition to other products.

3. The structure of the bisulfite compound corresponds to 3,4-dihydro-1,2-phenanthrenequinone-1-oxime-4-sulfonic acid.

4. In an alkaline medium the oxime of the bisulfite compound is converted into 1,2-phenanthrenequinonedioxime and then into 1,2-phenanthrofurazan; oxidation of 1,2-phenanthrenequinonedioxime with nitric acid leads to 1,2-phenanthrofuroxan.

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DOUBLE ARYLDIAZONIUM CHLORIDES OF COLUMBIUM AND TANTALUM

V. M. Cherkasov and I. F. Vladimirtsev

Ural Polytechnic Institute
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2235-2238,
July, 1960
Original article submitted July 16, 1959

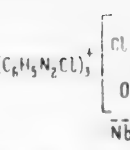
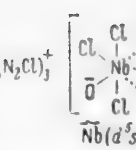
Alkyl and aryl organometallic derivatives of columbium and tantalum—as indeed of the majority of transition metals—have not previously been prepared. Existing literature data about the preparation of these compounds arouse serious doubts [1-3]. The preparation of organometallic compounds of vanadium, columbium and tantalum with the help of the diazo method (with decomposition of the double aryldiazonium salts with chlorides of these metals) has not been described in the literature. One of us [4] prepared double aryldiazonium salts with vanadium chloride [4].

The objective of the present work was the preparation of double aryldiazonium salts with columbium pentachloride and tantalum pentachloride. In order to clarify the effect of electron-donating and electron-accepting substituents on the properties of double diazonium salts, diazonium chlorides with various aryls (phenyl, o- and p-anisyl and p-nitrophenyl) were brought into reaction with columbium pentachloride.

The very marked susceptibility of columbium pentachloride to hydrolysis with formation of columbium oxychloride is mentioned in most literature sources (for example [5,6]). In presence of atmospheric moisture yellow columbium pentachloride does indeed rapidly change color and evidently forms the white columbium oxychloride which is more resistant to hydrolysis and does not undergo further hydrolysis during reactions in anhydrous alcoholic-ethereal media. Therefore in place of the proposed double diazonium salts on the basis of columbium pentachloride the double salts were obtained with columbium oxychloride.

o- and p-anisyldiazonium chlorides were brought into reaction with columbium pentachloride in 2:1 molar ratios to form double salts with the constant composition $(CH_3OC_6H_4N_2Cl)_2 \cdot NbOCl_3$. In order to establish to what extent the composition of the salts is constant, o-anisyldiazonium salt and columbium pentachloride were brought into reaction in equimolar ratio, and a salt of the above composition was obtained in nearly quantitative yield, while the mother liquor contained 50% of columbium pentachloride which had not reacted.

In analogy with the salt of columbium oxychloride and cesium chloride [7] $NbOCl_3 \cdot 2\,CsCl$, the formula $[CH_3OC_6H_4N_2Cl]_2 \cdot NbOCl_3$ corresponds to the coordination formula $[CH_3OC_6H_4N_2]_2^+ \left[\begin{matrix} O & Cl \\ ClNbCl \\ Cl & Cl \end{matrix}\right]^{2-}$ with a columbium coordination number of 7. The double salt of phenyldiazonium chloride with columbium oxychloride $(C_6H_5N_2Cl)_3 \cdot NbOCl_3$ was prepared with starting components in 2:1 ratio. A salt of variable composition was obtained if the starting components were taken in ratios of 3:1 and 1:1 (in the former case with a higher content of diazonium salt and in the latter case with a higher content of columbium oxychloride). The variable composition of the salt is evidently governed by the influence of the substituents in the aryl on the coordination number of the metal and on the coordinative capacity of oxygen. Two coordination formulas can be proposed for the salt $(C_6H_5N_2Cl)_3 \cdot NbOCl_3$:

$(C_6H_5N_2Cl)_3^+$ []$^{3-}$ and $(C_6H_5N_2Cl)_3^+$ []$^{3-}$

$\widetilde{Nb}(d^5sp^3)$ $\widetilde{Nb}(d^5sp)$

In the first formula columbium has the coordination number of 8, which is improbable since compounds of columbium with this coordination number are unknown. In the second formula the coordination number of columbium is 7 with oxygen coordination capacity of 1. A double diazonium salt is not usually detected when p-nitrophenyldiazonium chloride is reacted with columbium pentachloride. Similarly no double salt is found after reaction with vanadium chloride, although other double diazonium salts with vanadium chloride are considerably more stable than the corresponding double diazonium salts with columbium oxychloride.

The salts obtained are in the form of nearly colorless crystals, very hygroscopic and quickly decomposing at above 0°. Salts with o- and p-anisyldiazonium chlorides are more resistant to hydrolysis and thermal treatment. Introduction of the electron-donating methoxyl group into the phenyl radical thus increases the stability of double diazonium salts with columbium oxychloride as well as the corresponding salts with vanadium chloride. According to the literature [8] for salts of heavy metals, on the other hand, the electron-accepting nitro group enhances the stability of double diazonium salts.

Numerous attempts at preparation under the same conditions of aryldiazonium salts with tantalum pentachloride were unsuccessful. Mixing of alcoholic-ethereal solutions of p-anisyldiazonium chloride with tantalum pentachloride led to separation of an oily product that could not be made to crystallize. The product has the properties of double diazonium salts: it decomposes with deflagration (slow decomposition is accompanied by nitrogen release), and is easily hydrolyzed with separation of tantalic acid gel. Dissolution of tantalum pentachloride in absolute alcohol is accompanied by heat liberation and evolution of hydrogen chloride, probably due to alcoholysis. The literature [9] actually reports that dissolution of tantalum pentachloride in the cold in anhydrous alcohol gives esters of tantalic acid chlorides. On the assumption that the small quantities of tantalic acid esters formed during dissolution of tantalum pentachloride in anhydrous alcohol hinder the crystallization of the resulting double diazonium salt, reactions were subsequently carried out in solutions in acetone or carbon disulfide; but crystalline salts were not obtained.

According to the literature [9], an ester of tantalic acid chloride $TaCl_2(OC_2H_5)_3$, is formed when tantalum pentachloride dissolves in absolute alcohol in the cold. This ester can be obtained in the solid form after distillation of the alcohol and drying in vacuo. This substance was isolated and brought into reaction with p-anisyldiazonium chloride. In this case an oily product is likewise obtained in alcoholic-ethereal solutions. Performance of the reaction in acetone solution yielded a crystalline precipitate with the properties of double diazonium salts but which on analysis was found to contain chlorine, nitrogen and tantalum in amounts not consistent with the formula $[p\text{-}CH_3OC_6H_4N_2Cl]_x \cdot [TaCl_2(OC_2H_5)_3]_y$ with various ratios of components.

Reaction of phenyldiazonium chloride with tantalum pentachloride was carried out in alcohol-ether solutions; in all cases the phenyldiazonium chloride was recovered in admixture with a minute quantity of tantalum pentachloride.

Formation of double diazonium salts with tantalum pentachloride is probably hindered by the circumstance that salts of pentavalent tantalum are very much more susceptible to hydrolysis than salts of columbium.

EXPERIMENTAL

Starting substances. Columbium pentachloride was prepared from columbium pentoxide [10] by heating in sealed tubes with carbon tetrachloride. The columbium pentoxide consisted of 99.5% Nb_2O_5 and 0.47% TiO_2. Tantalum pentachloride was prepared by chlorination of metallic tantalum (99.5%) in a quartz tube at 350° [5].

Reaction of p-anisyldiazonium chloride with columbium pentachloride. Preparation of the double salt of p-anisyldiazonium chloride with columbium oxychloride. To a suspension of 3.2 g (0.012 mole) of columbium pentachloride in 30 ml of absolute ether at 0° was added 12 ml of anhydrous alcohol.

A solution of 3.8 g (0.024 mole) of p-anisidine hydrochloride in 18 ml of absolute alcohol was diazotized at 0° with 6 ml of isoamyl nitrite.

At 0° a solution of columbium pentachloride was added to the diazonium salt solution; the solution became brown and a precipitate came down. The mixture was stood at 0° for 20-30 min (rigorous exclusion of moisture is necessary). The precipitate was filtered quickly (with exclusion of bubbles of air), and washed several times with anhydrous alcohol–ether mixture for removal of traces of isoamyl nitrite. The resulting product was dried in a vacuum-desiccator over phosphorus pentoxide. Yield 4.6-5.3 g (69-80%). The salt formed greenish-gray crystals, poorly soluble in anhydrous alcohol and acetone, insoluble in ether, readily soluble in water; it hydrolyzes rapidly with separation of columbic acid.

It decomposes with deflagration at 145-146°. In absence of moisture it can be stored in a refrigerator without appreciable breakdown for 3-4 weeks. A freshly prepared product must be taken for analysis. Nitrogen was determined by the Dumas method, columbium by the gravimetric method as Nb_2O_5, and chlorine by the volumetric mercurimetric method [11].

Found %: N 10.48, 10.58; Cl 31.55, 31.58; Nb 17.12, 16.97. $(p\text{-}CH_3OC_6H_4N_2Cl)_2 \times NbOCl_3$. Calculated %: N 10.07; Cl 31.90; Nb 16.69.

Reaction of o-anisyldiazonium chloride with columbium pentachloride. Double salt of o-anisyldiazonium chloride and columbium oxychloride. Prepared along the same lines as the previous salt with p-anisyldiazonium chloride. Starting components were 1.08 g (0.004 mole) of columbium pentachloride, dissolved in a mixture of 10 ml of absolute ether and 1 ml of anhydrous alcohol, and 1.2 8 g (0.008 mole) of o-anisidine hydrochloride in 6 ml of anhydrous alcohol. Diazotization of the mixture was effected with 2 ml of isoamyl nitrite. Yield 1.4 g (68.5%). A crystalline substance with a yellowish tinge. It had all the properties of the p-anisyldiazonium salt. It decomposed with deflagration in a test tube at 140°.

Found %: N 9.87 9.56; Cl 31.43, 31.59; Nb 17.24, 17.22. $(o\text{-}CH_3OC_6H_4N_2Cl)_2 \times NbOCl_3$. Calculated %: N 10.07; Cl 31.90; Nb 16.69.

Same reaction with 1:1 ratio of reactants. From 1.08 g (0.004 mole) of columbium pentachloride and 0.65 g (0.004 mole) of o-anisidine hydrochloride was obtained 1.05 g (95 4%) of the double salt of o-anisyldiazonium chloride with columbium oxychloride.

Found %: N 10.46; Cl 31.43; Nb 17.04.

Phenyldiazonium reaction with columbium pentachloride. Double salt of phenyldiazonium chloride and columbium oxychloride. Prepared by the previous procedure from 1.1 g (0.008 mole) of aniline hydrochloride (suspension in 5 ml of anhydrous alcohol), diazotized with 1.6 ml of isoamyl nitrite, and 1.0 8 g (0.004 mole) of columbium pentachloride in solution in anhydrous alcohol-ether. Yield 1.3 g (81.2% calculated on the aniline hydrochloride). The salt forms fine, light, pale-yellow crystals, easily soluble in water. It quickly hydrolyzes. Decomposes with detonation in a test tube at 85-86° It is considerably less stable than the salts with anisyldiazonium. It breaks down appreciably after a few days under the same storage conditions.

Found %: N 13.28; Cl 32.97, 33.09; Nb 14.35, 14.40. $(C_6H_5N_2Cl)_3 \cdot NbOCl_3$. Calculated %: N 13.18; Cl 33.44; Nb 14.58.

SUMMARY

1. Reaction of aryldiazonium chlorides with columbium pentachloride leads to formation of compounds of aryldiazonium salts with columbium oxychloride due to hydrolysis.

2. It is shown that replacement of a hydrogen in a phenyl group by an electron-donating group (CH_3O) improves the stability of the double diazonium salts with columbium oxychloride, while introduction of an electron-accepting group (NO_2) generally prevents formation of a double diazonium salt.

3. It is shown that double salts of aryldiazonium salts with tantalum pentachloride are not formed under similar conditions.

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*Original Russian pagination. See C. B. translation.

INVESTIGATIONS OF CONJUGATED SYSTEMS

CXX. ADDITION OF ALKYLLITHIUMS TO VINYLISOPROPENYLACETYLENE*

A. A. Petrov, V. A. Kormer, and T. V. Yakovleva

Leningrad Lensovet Institute of Technology

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2238-2243, July, 1960
Original article submitted July 16, 1959

Earlier investigations in our laboratory established that alkyllithiums add on with facility to vinylalkylacetylenes with formation (after treatment of the reaction mixture with water) of symmetrically disubstituted allenes (1,4-addition). Telomerization practically does not occur if the reaction is performed at low temperatures. We attributed this behavior to the poor reactivity of the resulting organolithium compounds with a lithium atom at the double bond in comparison with the reactivity of the original alkyllithiums [1].

It was interesting to establish the sequence of addition of alkyllithiums to hydrocarbons containing a more extended conjugated chain of double bonds, in particular to dienic hydrocarbons. Here we could expect formation of 1,2-, 1,4- and 1,6-adducts. Addition of radicals to the central carbon atoms was hardly probable and has never been observed [2].

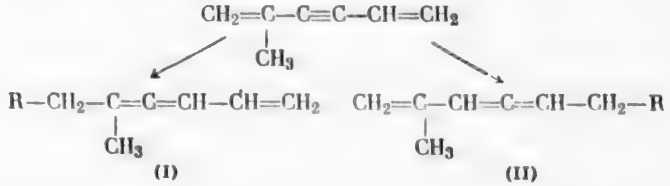
$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{R{-}Li,\ H_2O} \begin{cases} \rightarrow CH_2{=}CH{-}C{\equiv}C{-}CH_2{-}CH_2{-}R & (1,2\text{-adduct}) \\ \rightarrow CH_2{=}CH{-}CH{=}C{=}CH{-}CH_2{-}R & (1,4\text{-adduct}) \\ \rightarrow CH_3{-}CH{=}C{=}C{=}CH{-}CH_2{-}R & (1,6\text{-adduct}) \end{cases}$$

It has already been reported in a short communication that alkyllithiums actually add on to divinylacetylene in the 1,4-position with formation of vinylallenic hydrocarbons [3].

The structure of the latter was verified by their infrared spectra (absorption bands of vinyl groups and of the allenic system were found but bands of the acetylenic bond were not detected) and by hydrogenation to the corresponding saturated hydrocarbons.

In the present communication we consider the addition of alkyllithiums to the nearest homolog of divinylacetylene—vinylisopropenylacetylene (2-methyl-1,5-hexadien-3-yne).

Unlike divinylacetylene, vinylisopropenylacetylene has an unsymmetrical structure. Addition of an alkyl can take place here at the vinyl or at the vinyl or at the isopropenyl group with formation of vinyl- and isopropenylallenic hydrocarbons (I) and (II).



(I) (II)

* Dienynes. IV.

The existence of a dipole moment in vinylisopropenylacetylene is evidence of a shift of the electron density in its molecule, evidently in the direction of the isopropenyl group [4]. Electrophilic addition of alkyl hypobromites to vinylisopropenylacetylene actually takes place at this group [5]. Alkyllithiums contain a strongly polarized covalent bond and the radical is anionoidic in character [6]. In the light of these considerations, we should expect addition of radicals to the electron-deficient vinyl group.

Such an order of addition of alkyllithiums could be predicted on the basis of the radical nature of the process. The methyl group screens the double bond in the isopropenyl group, and radical processes are extremely sensitive to the action of steric factors.

Addition of alkyllithiums actually took place nearly exclusively at the vinyl group.

In the infrared spectrum of the original hydrocarbon the vinyl group is represented by extremely strong deformed frequencies at 920 and 967 cm^{-1} and the isopropenyl group by the 890 cm^{-1} frequency [5]. In the spectra of the hydrocarbons prepared from vinylisopropenylacetylene by addition of alkyllithiums, the frequencies of the vinyl group are substantially absent but the frequency of the isopropenyl group is retained (Fig. 1).* In the region of valence vibrations of the double bonds, strong absorption is observed only at 1620-1630 and 1940 cm^{-1}. The hydrocarbons consequently have the structure (II), i.e., they are isopropenylallenes.

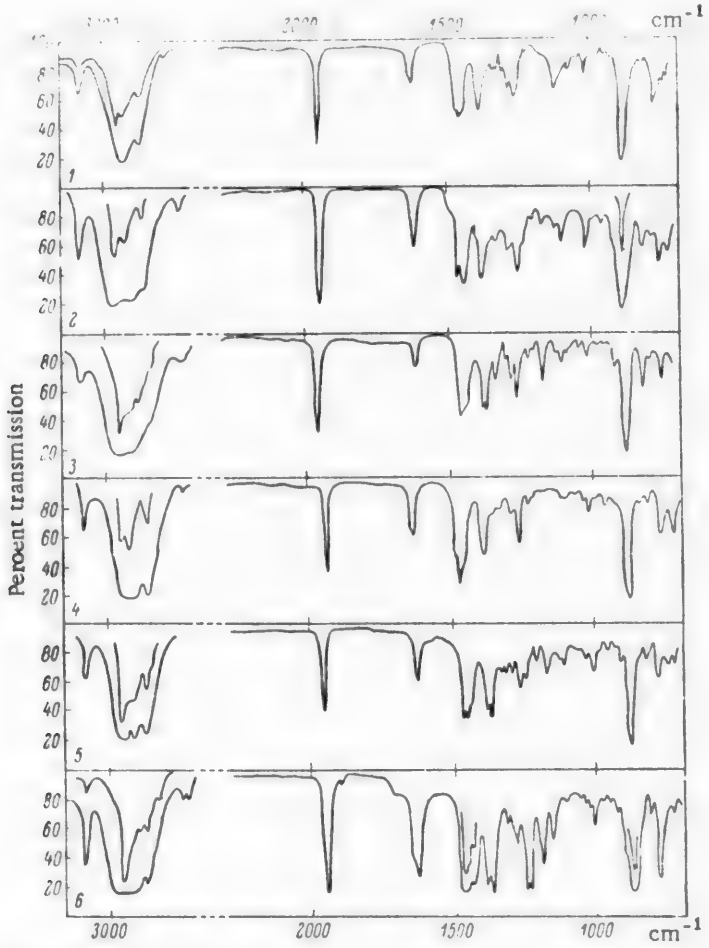


Fig. 1. Infrared transmission spectra; 1) 2-methyl-1,3,4-octatriene, 2) 2-methyl-1,3,4-nonatriene, 3) 2,7-dimethyl-1,3,4-octatriene, 4) 2-methyl-1,3,4-decatriene, 5) 2,3-dimethyl-1,3,4-nonatriene, 6) 2,7,7-trimethyl-1,3,4-octatriene.

* The extremely feeble frequencies in the 900-1000 cm^{-1} region can only be associated with a very small trace of vinyl compounds in the basic substance (of the order of 5%). These frequencies might also be overtones or may relate to chain vibrations.

Constants and Analytical Data for Isopropenylallenes

Substance	Empirical formula	Boiling point (pressure 20 mm)	d_4^{20}	n_D^{20}	MR found	MR calculated	Found (%) C	Found (%) H	Calculated (%) C	Calculated (%) H	Yield (%)	Distillation residue (in g)
$CH_2=C(CH_3)-CH=C=CH-CH_2-C_2H_5$	C_9H_{14}	54—55°	0.7775	1.4790	44.57	42.36	88.23, 87.67	11.75, 11.75	88.45	11.55	77	1.3
$CH_2=C(CH_3)-CH=C=CH-CH_2-C_3H_7$	$C_{10}H_{16}$	71—72	0.7834	1.4790	49.31	46.98	88.00, 87.94	11.74, 11.82	88.16	11.84	70	1.8
$CH_2=C(CH_3)-CH=C=CH-CH_2-CH(CH_3)_2$	$C_{10}H_{16}$	67.5—68.5	0.7793	1.4750	49.22	46.98	87.92, 87.94	11.92, 11.98	88.16	11.84	72	3.6
$CH_2=C(CH_3)-CH=C=CH-CH_2-C_4H_9$	$C_{11}H_{18}$	89.5—90.5	0.7898	1.4795	54.00	51.60	87.74, 88.06	12.27, 12.35	87.92	12.08	77	2.0
$CH_2=C(CH_3)-CH=C=CH-CH_2-CH_2-CH(CH_3)_2$	$C_{11}H_{18}$	83—83.5	0.7853	1.4762	53.99	51.60	87.86, 87.94	12.20, 12.22	87.92	12.08	76	1.7
$CH_2=C(CH_3)-CH=C=CH-CH_2-C(CH_3)_3$	$C_{11}H_{18}$	76.5—77.5	0.7852	1.4719	54.12	51.60	87.60, 87.43	12.33, 12.31	87.92	12.08	46	3.0

This conclusion about the structure of the adducts was also confirmed by ozonolysis reactions. Ozonization of the hydrocarbons gave the corresponding carboxylic acids. Carbonyl compounds were obtained in quantities indicating the presence of a small proportion of isomers of (I)

Isopropenylallenes are colorless liquids with a characteristic unpleasant odor, turning yellow after prolonged storage. Introduction of a more branched radical results in decrease in boiling points, specific gravities and refractive indices. The magnitude of the exaltation of molecular refraction is here larger than in the case of vinylallenes (2.3-2.4).

The infrared spectra of vinyl- and isopropenylallenes differ in several respects from those of disubstituted allenes [7].

The spectra of vinylallenes (Fig. 2) contain the fairly strong valence vibration frequency of the double bond at 1615 cm^{-1} and extremely strong deformed CH-vibration bands of the vinyl group at 990 and 895 cm^{-1}.

All these are absent from the spectra of disubstituted allenes. A similar deformation band of the allenic grouping (878 cm^{-1}) is observed as an extension on the considerably more intense 895 cm^{-1} band.

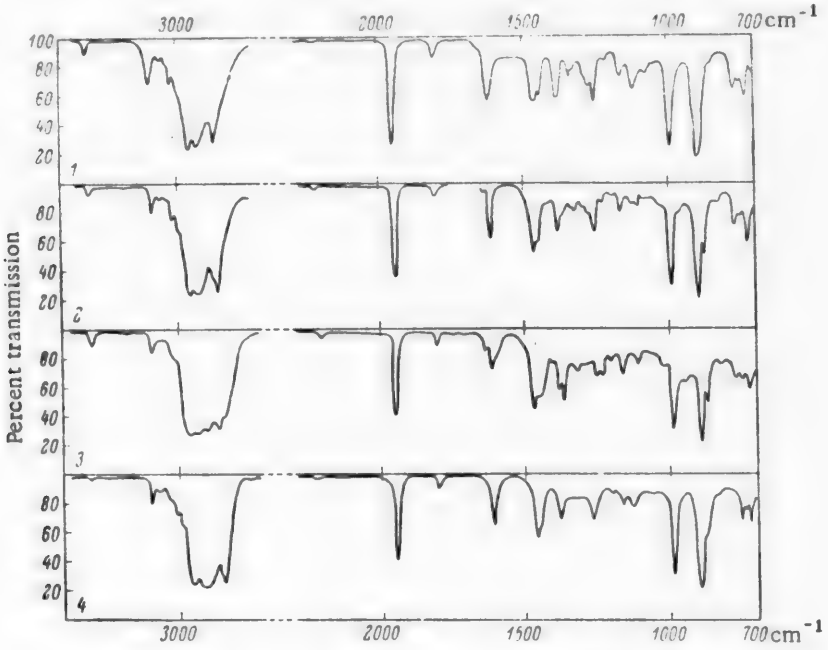


Fig. 2. Infrared transmission spectra; 1) 1,3,4-octatriene, 2) 1,3,4-decatriene, 3) 8-methyl-1,3,4-nonatriene, 4) 1,3,4-undecatriene.

The characteristic frequencies of the conjugated $CH_2=CR_2$ grouping (3100, 1615 and 840 cm^{-1}) appeared in the infrared spectra of isopropenylallenes (Fig. 1). The 880 cm^{-1} frequency, characteristic of disubstituted allenes, is here not differentiated. With increasing branching of the radical added to the conjugated system, the absorption increases in the 1200 cm^{-1} region.

EXPERIMENTAL

To an ethereal solution of alkyllithium, prepared from 6 g of lithium and 0.4 mole of alkyl chloride in 400 ml of ether at -35°, was added about 0.1 mole of vinylisopropenylacetylene with good mechanical stirring. After the lapse of 20-60 min, the reaction mixture was treated with water and fractionally distilled. Results of some experiments and the analytical data are set forth in the table.

Ozonolysis of 2.9 g of the hydrocarbon obtained from vinylisopropenylacetylene and butyllithium gave a mixture of acids and a small quantity of carbonyl compounds (in the form of 2,4-dinitrophenylhydrazone – 0.6 g). Among the acids were found formic (by calomel test) and butyric (nitroprusside test and odor) acids [8].

We were able to isolate the 2,4-dinitrophenylhydrazone of methyl propyl ketone from the mixture of dinitrophenylhydrazones. This ketone must have been formed by ozonolysis of the isomer of (I).

SUMMARY

1. The sequence of addition of alkyllithiums to vinylisopropenylacetylene was investigated.

2. It was shown that alkyl radicals are added preferentially from the side of the vinyl group with formation of isopropenylallenes.

3. Some special features of the infrared spectra of vinylacetylenic and isopropenylallenic hydrocarbons were noted.

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INVESTIGATIONS OF CONJUGATED SYSTEMS

CXXI. ADDITION OF ALKYLLITHIUMS TO TRIALKYLVINYLETHYNYLSILANES*

A. A. Petrov, V. A. Kormer, and M. D. Stadnichuk

Leningrad Lensovet Institute of Technology

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2243-2248, July, 1960
Original article submitted July 16, 1959

Vinylacetylenic hydrocarbons (disubstituted acetylenes) readily add on alkyllithiums with formation (after treatment of the reaction mixture with water) of allenic hydrocarbons [1]. Under similar conditions divinylacetylenic hydrocarbons give alkenylallenes [2]. The yield of allenes exceeds 70% if this reaction is performed at low temperature in ether, and hardly any high-boiling products are formed.

Continuing the study of reactions of alkyllithiums with compounds containing an enynic system of bonds, we became interested in the reaction of alkyllithiums with silicon-containing vinylacetylenes, and first of all with trialkylvinylethynylsilanes. The presence of a silicon atom in a conjugated system could easily alter the sequence of addition of alkyllithiums since the carbon–silicon bond differs appreciably in character from the carbon–carbon bond and approximates to a double bond [3].

In the literature on this subject we found only one paper by Petrov, Sadykhzade and Egorov [4] on the action of methyllithium on trimethylvinylethynylsilanes and of butyllithium on triethylvinylethynylsilane. These authors concluded that the reaction products are acetylenic compounds. The Raman spectrum of the resulting organosilicon compounds actually contained a triple-bond frequency.

We have investigated the addition to trimethylvinylethynylsilane of ethyllithium, propyllithium, isopropyllithium, butyllithium and tert-butyllithium. After the reaction product had been treated with water, adducts of the anticipated composition $(CH_3)_3Si-C_4H_4-R$ were obtained in all cases.

Depending on the order of addition of the alkyllithiums, they can have the following structure:

$(CH_3)_3Si-C\equiv C-CH_2-CH_2-R$ (I)

$(CH_3)_3Si-CH=C=CH-CH_2-R$ (II)

$(CH_3)_3Si-C\equiv C-\underset{\displaystyle R}{\underset{|}{CH}}-CH_3$ (III)

$(CH_3)_3-Si-\underset{\displaystyle R}{\underset{|}{C}}=CH-CH=CH_2$ (IV)

$(CH_3)_3Si-\underset{\displaystyle R}{\underset{|}{C}}=C=CH-CH_3$ (V)

$(CH_3)_3Si-CH=\underset{\displaystyle R}{\underset{|}{C}}-CH=CH_2$ (VI)

The infrared spectra of all of the adducts contained valence vibration frequencies of the triple bond (2175 cm^{-1}) and of the allenic bond system (1938 cm^{-1}). In the spectral region characterizing the valence vibrations of double bonds, no absorption was observed (Fig. 1). These data indicate that the adducts in question are mixed acetylenic and allenic compounds and that formulas (IV) and (VI) can be rejected.

* Enynic compounds. XLII.

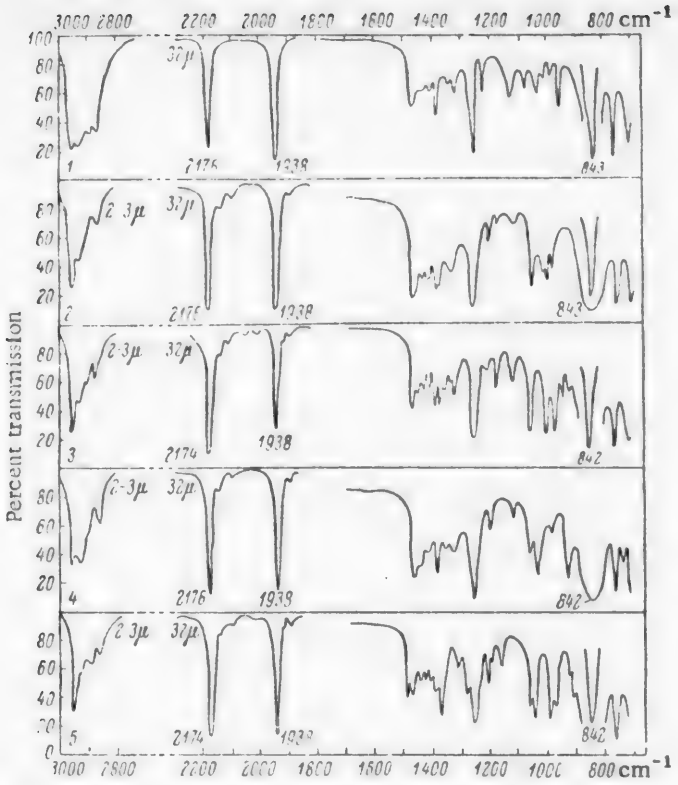

Fig. 1. Infrared transmission spectra of silicohydrocarbons obtained from products of addition to trimethylvinylethynylsilane: 1) ethyllithium, 2) propyllithium, 3) isopropyllithium, 4) butyllithium, 5) tert-butyllithium.

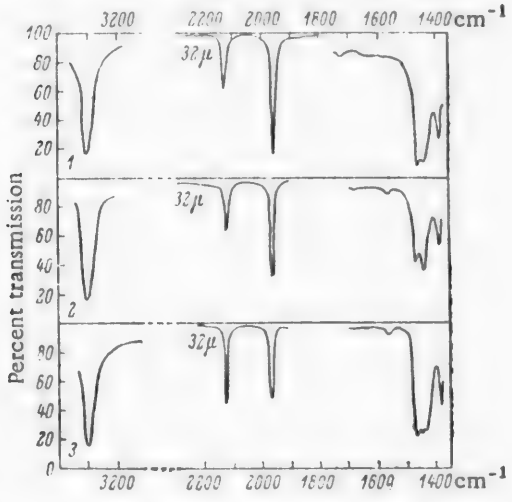

Fig. 3. Infrared transmission spectra of hydrocarbons obtained by hydrolysis of the adducts; 1) ethyllithium (45% of acetylene), 2) ethyllithium (48% acetylene), 3) butyllithium.

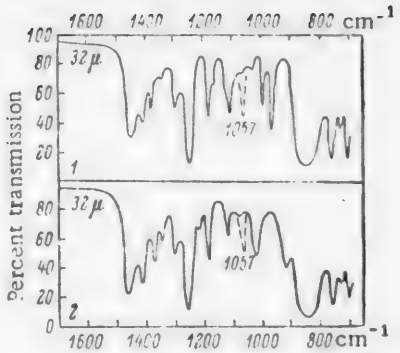

Fig. 2. Infrared transmission spectra; 1) trimethylhexylsilane, 2) trimethyloctylsilane (the dashed plot relates to the frequency of specimens obtained via the organomagnesium compounds).

Hydrogenation over $Pd/CaCO_3$ of silicohydrocarbons prepared from the ethyllithium and butyllithium adducts gave trimethylhexyl- and trimethyloctylsilane respectively. The structure of the latter was verified by comparison of their infrared spectra with the spectra of authentic specimens of these silicohydrocarbons (Fig. 2). Consequently, all formulas except (I) and (II) are excluded.

The ratio between acetylenic and allenic isomers was determined on the basis of hydrolysis data. The ratio could also be evaluated from the intensities of the 1938 and 2176 cm^{-1} bands in the infrared spectra (Fig. 3) and from the magnitude of the molar refraction.

Hydrolytic cleavage of the two silicohydrocarbons with $R = C_2H_5$ and C_4H_9 gave hexamethyldisiloxane and mixtures of acetylenic and allenic hydrocarbons with the composition C_6H_{10} and C_8H_{14} (see scheme below).

Allene–acetylene isomerization was excluded here because hydrolysis was carried out at 65-70°.

The content of acetylenic isomer in the mixture was determined analytically [5]. It varied slightly from one experiment to another. Some data are presented in the table.

The calculated values of molar refraction for the allenic isomer (II) are 0.67 higher than those of the acetylenic isomer (I). Judging by the tabulated data, the pure allenic isomers must have an exaltation of the order of 1.25. These data enable calculation of the probable composition of mixtures of adducts (I) and (II).

$$(I) \longrightarrow HC{\equiv}C{-}CH_2{-}CH_2{-}R + (CH_3)_3Si{-}O{-}Si(CH_3)_3$$

$$(II) \longrightarrow CH_2{=}C{=}CH{-}CH_2{-}R + (CH_3)_3Si{-}O{-}Si(CH_3)_3$$

It has consequently been demonstrated that alkyllithiums add on to trimethylvinylethynylsilane with formation of a mixture of allenic and acetylenic compounds, i.e., a result different from that obtained with the analogously constructed vinylalkylacetylenes. The change in order of addition is evidently caused by triple bond electron interaction with the outer shell of the silicon atom and by steric factors.

$$(CH_3)_3Si-C\equiv C-CH=CH_2$$

Allenic isomers were not detected by the previously mentioned investigators [4], probably because the Raman spectra used for verification of structure do not always definitely exhibit the frequencies characteristic of the allenic grouping. Judging by the value of the molar refraction, the methyllithium adduct contained about 90% of acetylenic isomer, whereas the butyllithium adduct contained only about 55%.

The course of the curve of rate of hydrogenation of mixtures of adducts (I) and (II) is noteworthy. As we see from Fig. 4, the first hydrogen molecule is taken up with accelerating speed, while the second molecule combines at a very much slower rate.

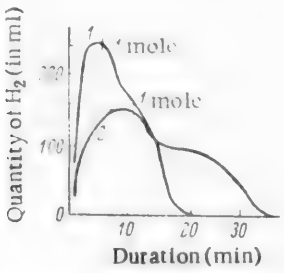

Fig. 4. Hydrogenation rate curves for silicohydrocarbons obtained from products of addition of ethyllithium (1) and butyllithium (2) to trimethylvinylethynylsilane.

EXPERIMENTAL

To a solution of alkyllithium, prepared from 6 g of lithium and 0.4 mole of the corresponding alkyl chloride in 400 ml of ether, was added about 0.1 mole of trimethylvinylethynylsilane at -35° with good stirring. After 20-30 min, the reaction mixture was treated with water and fractionally distilled. The constants of the products, their yields and analytical data are set forth in the table.

a) Hydrogenation of 5.93 g of the substance obtained by addition of ethyllithium over 5 g of $Pd/CaCO_3$ in 30 ml of methanol led after 40 min to absorption of 864 ml of H_2 (768.5 mm, 27°), which is equivalent to 90% of the theoretical amount. The reaction mixture was diluted with water and distilled until the residue was nearly dry. Salting-out of the distillate with saturated $CaCl_2$ solution gave trimethylhexylsilane (81%) with b.p. 162.5-163.5°, d_4^{20} 0.7424, n_D^{20} 1.4154. The infrared spectrum of the substance is shown in Fig. 3.*

Reaction of trimethylchlorosilane with an ethereal solution of hexylmagnesium bromide gave the same trimethylhexylsilane with b.p. 162.5-163.5°, d_4^{20} 0.7467, n_D^{20} 1.4152. The infrared spectrum of the substance differed from the spectrum of the product of hydrogenation only in respect of the stronger absorption in the 1057 cm^{-1} region which reflected the presence of siloxane as impurity (for which this frequency is extremely characteristic [6]).

b) Hydrogenation of the silicohydrocarbon obtained by addition of butyllithium gave trimethyloctylsilane with b.p. 202-206°, d_4^{20} 0.7567, n_D^{20} 1.4242. The infrared spectrum of the substance is shown in Fig. 3.

The same product was obtained by the organomagnesium synthesis and had b.p. 201-203°, d_4^{20} 0.7612, n_D^{20} 1.4248.

As in the first case the infrared spectrum of the substance differed from that of the product of hydrogenation only in respect of the greater intensity of absorption at 1057 cm^{-1}

It should be noted that the constants found for trimethylalkylsilanes very closely approach those reported for these compounds in the literature [7].

Hydrolytic cleavage. a) The ethyllithium adduct (3.2 g) was heated until fully dissolved in 10% KOH solution in methanol (about 1.5 hr). The mixture was then diluted with water and distilled until the temperature reached 100°. Treatment of the distillate with saturated $CaCl_2$ solution yielded 2.7 g of hexamethyldisiloxane and a mixture of allenic and acetylenic hydrocarbons with b.p. 72-76°, d_4^{20} 0.7276, n_D^{20} 1.4008. The infrared spectrum of this compound is shown in Fig. 3.

Acetylenic hydrocarbon found (%): 44.1, 46.0.

* The authors convey thanks to T. V. Yakovleva for assistance in the investigation of the infrared spectra.

Constants and Analytical Data for Silicohydrocarbons

$(CH_3)_3-Si-CH=C=CH-CH_3-R$ / $(CH_3)_3-Si-C\equiv C-CH_2-CH_2-R$ R	Boiling point (50 mm)	d_4^{20}	n_D^{20}	MR found	MR calculated acetylene	MR calculated allene	Acetylene content found	Acetylene content calculated	Found (%) C	Found (%) H	Found (%) Si	Empirical formula	Calculated (%) C	Calculated (%) H	Calculated (%) Si	Yield (%)
C_2H_5 (expt. 1)	59°	0.7696	1.4402	52.82	51.82	52.49	46.0, 44.1	45.8	69.54	11.86	17.30, 17.51	$C_9H_{18}Si$	70.06	11.76	18.18	76.6
C_2H_5 (expt. 2)	59	0.7694	1.4390	52.73	51.82	52.49	48.4, 47.6	45.8	—	—	—	—	—	—	—	66.7
C_3H_7	75—76	0.7722	1.4402	57.47	56.45	57.12	—	46.9	70.67	12.70	—	$C_{10}H_{20}Si$	71.35	11.98	—	86.0
iso-C_3H_7	70—71	0.7700	1.4357	57.09	56.45	57.12	—	46.6	70.70	12.22	16.57	$C_{10}H_{20}Si$	71.35	11.98	16.67	69.3
C_4H_9 (expt. 1)	91—92	0.7785	1.4432	62.11	61.08	61.75	—	46.4	—	—	—	—	—	—	—	68.5
C_4H_9 (expt. 2)	91—92	0.7797	1.4404	61.69	61.08	61.75	78.0, 76.6	68.0	72.11, 72.74	12.25, 12.37	15.99, 15.32	$C_{11}H_{22}Si$	72.45	12.16	15.39	63.2
tert.-C_4H_9	81—82	0.7771	1.4420	62.09	61.08	61.75	—	47.3	73.08	12.38	15.52, 14.69	$C_{11}H_{22}Si$	72.45	12.16	15.39	74.0

b) Cleavage under similar conditions of the silicohydrocarbon from the butyllithium adduct gave a mixture of allenic and acetylenic hydrocarbons with b.p. 122-126°, d_4^{20} 0.7512, n_D^{20} 1.4112.

Acetylenic hydrocarbon found (%): 78.0, 78.6.

SUMMARY

1. The reaction of alkyllithiums with trimethylvinylethynylsilane was investigated.

2. It was shown that in all cases acetylenic and allenic adducts are formed. The structure of the adducts was established by hydrogenation to the corresponding saturated silicohydrocarbons, by hydrolytic cleavage to hydrocarbons and from the infrared spectra.

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INVESTIGATIONS ON CONJUGATED SYSTEMS

CXXII. DIPOLE MOMENTS AND REACTIVITIES OF VINYLACETYLENIC KETONES AND AMINES*

A. A. Petrov, K. S. Mingaleva, I. A. Maretina, and V. D. Nemirovskii

Leningrad Lensovet Institute of Technology

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2248-2250, July, 1960
Original article submitted July 16, 1959

The concept of electron density shift in the 1,3-enynic system under the influence of radicals [1-3] has been used to explain the differing reactivities of vinylacetylenic hydrocarbons in a series of investigations in our laboratory. The existence of such a shift was confirmed by various methods, including dipole moment measurements [4]. For a similar interpretation of the characteristics of the reactivity of derivatives of vinylacetylenic hydrocarbons, it was necessary to have data for their dipole moments. The data in question are not found in the literature.

We determined the dipole moments of two vinylacetylenic ketones of different structures (I) and (II) and of amine (III).

The dipole moment of the vinylacetylenic ketone (I) was considerably larger than the moments of methyl vinyl ketone (2.98 D) [5] and mesityl oxide (2.84 D) [6]. In the molecule of (I) the electronic density shift under the influence of the carbonyl group proceeds in the same direction as in the vinylacetylene system. The dipole moment of ketone (II), with the opposite direction of the moments of the carbonyl group and of the enynic system, was smaller than that of methyl vinyl ketone (see Table 1). The same relation was found between the polarizabilities of these ketones (see Table 2).

TABLE 1.

Substance	ξ_0	U_0	α	$-\beta$	P_∞	Dipole moment (D)
$CH_3-CO-C\equiv C-CH=CH_2$	2.283	1.1368	12.45	0.035	249.03	3.24
$CH_3-CO-CH=CH-C\equiv CH$	2.284	1.1368	8.66	0.061	182.10	2.71
$HC\equiv C-CH=CH-N(C_2H_5)_2$	2.283	1.1367	7.50	0.034	212.64	2.87

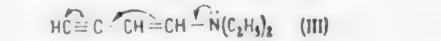
TABLE 2.

Substance	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR found	MR calculated	Literature
$CH_3-CO-C\equiv C-CH=CH_2$	35° (10)	0.9081	1.4840	29.65	27.45	[13]
$CH_3-CO-CH=CH-C\equiv CH$	56—57 (20)	0.9308	1.4928	29.37	27.45	[13]
$HC\equiv C-CH=CH-N(C_2H_5)_2$	53—54 (5)	0.9068	1.5208	41.36	40.62	[12]

* Enynic compounds. XLIII.

(I) (II)

The vinylacetylenic amine (III), in whose molecule conjugation takes place between the electron pair of the nitrogen atom and the enynic system, had an extremely large dipole moment, whereas saturated and unsaturated amines lacking this structure have small dipole moments [7]. The origin of the dipole moment in amine (III) is similar to that in the case of arylamines [8,9] and unsaturated aminoketones containing conjugated multiple bonds [10].



(III)

This agreement between the expected changes in dipole moments under the influence of conjugation and the experimental values demonstrate the soundness of our hypothesis of electron shifts in 1,3-enynic systems.

Addition reaction of derivatives of vinylacetylenic hydrocarbons have not been adequately investigated but certain conclusions have already been drawn.

Vinylacetylenic ketones add on bromine rather unselectively [11], possibly due to both electrophilic and nucleophilic bromination. Comparisons of the size of the dipole moments is not possible.

The vinylacetylenic amine (III) adds on bromine predominantly at the triple bond, which is consistent with the electronic polarization to be expected from the magnitude of the dipole moment [12]. A certain correlation can thus be established in some cases between polarity in the steady state and reactivity of derivatives of vinylacetylenic hydrocarbons.

EXPERIMENTAL

All of the investigated compounds were prepared by the literature methods and had constants close to those reported by other workers (Table 2).

The dipole moments were determined in dilute solutions in benzene. The permittivity was measured by the beat method with a TKE-1 instrument specially adapted for this purpose. Dipole moments were calculated in the usual manner. Experimental data needed for calculations are set forth in Table 1. No allowance was made for the atomic polarization.

SUMMARY

1. The dipole moments of 1-hexen-3-yn-4-one, 3-hexen-1-yn-4-one and 1-diethylamino-2-buten-1-yne were measured.

2. It was found that the postulated shifts of electron density in the investigated compounds are confirmed by the dipole moments found.

3. The data obtained were related to certain chemical properties of the investigated compounds.

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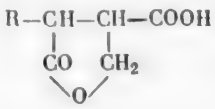
SYNTHESIS OF RACEMIC STEREOISOMERIC α-ALKYLPARACONIC ACIDS

N. A. Preobrazhenskii, M. E. Maurit, G. I. Bazilevskaya,
G. V. Smirnova, M. M. Él'manovich, A. I. Valakhanovich
and É. Persiyanova

Moscow Institute of Fine Chemical Technology
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2250-2256,
July, 1960
Original article submitted June 22, 1959

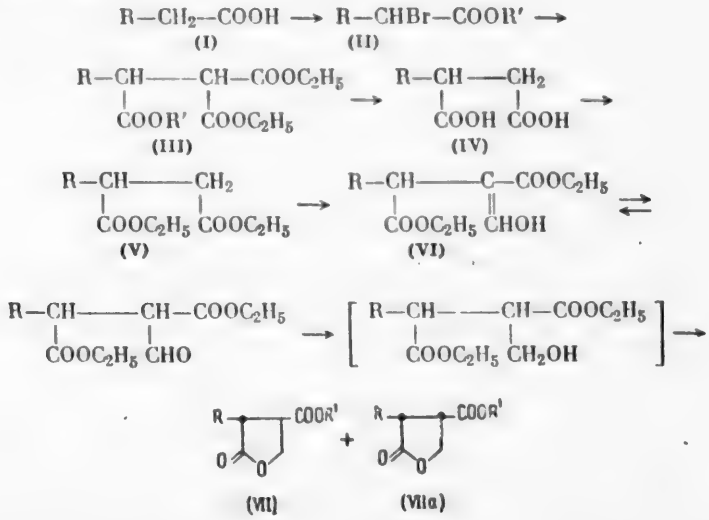
The butyrolactone grouping is found in the molecules of many derivatives of biologically active substances for example in cardiac glucosides, ascorbic acid, santonin, pilocarpine, etc.

In connection with our investigations of the synthesis of pilocarpine and its homologs, we studied the synthesis of α-alkyl-γ-butyrolactone-β-carboxylic acids (α-alkylparaconic acids).



Characteristic of these compounds is the existence of steric isomers due to the presence of two asymmetric carbons in the lactonic ring. Difficulties involved in resolution of spatial isomers are here further intensified by the very great susceptibility of the stereoisomers to rearrangements.

We carried out the synthesis of α-alkylparaconic acids containing various substituents in the α-position by the following series of reactions:



We introduced a number of simplifications and improvements into the synthesis of α-alkylparaconic acids and the starting substances; some of these compounds were not previously described in the literature, or their constants had not been fully reported. In this paper we therefore describe the preparation and properties of a series of α-alkylparaconic acids and their intermediate products.

EXPERIMENTAL

1. Esters of α-bromoaliphatic acids (II). Ethyl α-bromobutyrate (II, R = R' = C_2H_5). Treatment of 217 g of butyric acid (I, R = C_2H_5) with 253 g of thionyl chloride at 65-70° for 4 hr gave the acid chloride which by heating at 60-65° for 20-24 hr with 434 g of bromine was converted to the corresponding α-bromo derivative; addition to the latter of 156 g of alcohol gave ethyl α-bromobutyrate. Yield 374 g (77.8%). B.p. 69-71° (17 mm) [1].

Esters of α-bromopropionic (II, R = CH_3, R' = C_2H_5), α-bromovaleric (II, R = n-C_3H_7, R' = C_2H_5) and α-bromoisovaleric (II, R = iso-C_3H_7, R' = CH_3) acids were similarly prepared (Table 1).

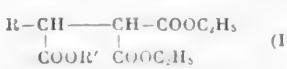
TABLE 1. Esters of α-Bromoacids R-CHBr-COOR' (II)

R	R'	Empirical formula	Boiling point (pressure in mm)	Yield (in %)	Literature
CH_3	C_2H_5	$C_5H_9O_2Br$	53–54° (17)	64.6	[2]
C_2H_5	C_2H_5	$C_6H_{11}O_2Br$	[illegible]	77.8	[1]
n-C_3H_7	C_2H_5	$C_7H_{13}O_2Br$	[illegible]	75.0	[1]
iso-C_3H_7	CH_3	$C_6H_{11}O_2Br$	[illegible]	71.6	[3]

2. Esters of α,α,β-alkyltricarboxylic acids (III). α,α,β-Butanetricarboxylic ester (III, R = R' = C_2H_5). Boiling of 374 g of α-bromobutyric ester (II, R = R' = C_2H_5) with an alcoholic solution of sodium malonic ester (prepared by addition of 337 g of ethyl malonate to 750 g of 17.35% alcoholic solution of sodium ethoxide) for 3-4 hr gave α,α,β-butanetricarboxylic ester. Yield 490 g (93.1%). B.p. 160-167° (18 mm) [4, 6].

Esters of α,α,β-propane-(III, R = CH_3, R' = C_2H_5), pentane-(III, R = n-C_3H_7, R' = C_2H_5) and isopentane-(III, R = iso-C_3H_7, R' = CH_3)tricarboxylic acids were similarly prepared (Table 2).

TABLE 2. Esters of α,α,β-Alkyltricarboxylic Acids


(III)

R	R'	Empirical formula	Boiling point (pressure in mm)	Yield (in %)	Literature
CH_3	C_2H_5	$C_{12}H_{20}O_6$	136–138° (7)	82.8	[4,5]
C_2H_5	C_2H_5	$C_{13}H_{22}O_6$	160–167 (18)	93.1	[4,6]
n.-C_3H_7	C_2H_5	$C_{14}H_{24}O_6$	144–148 (11)	70.2	[5]
iso-C_3H_7	CH_3	$C_{13}H_{22}O_6$	151–156 (13)	79.3	[3,5]

3. Alkylsuccinic acids (IV). Ethylsuccinic acid (IV, R = C_2H_5). A mixture of 490 g of α,α,β-butanetricarboxylic ester (III, R = R' = C_2H_5) and 1960 ml of 18% hydrochloric acid was boiled until the layers disappeared (10-12 hr). The solution was evaporated to dryness. Yield of ethylsuccinic acid (IV, R = C_2H_5) 260 g (99.6%).

Methyl-(IV, R = CH_3), propyl- (R = n-C_3H_7) and isopropyl- (R = iso-C_3H_7) succinic acid were prepared by saponification of the corresponding α,α,β-alkyltricarboxylic esters (III) (Table 3).

TABLE 3. Alkylsuccinic Acids

(IV)

R	Empirical formula	M.p. (solvent for recrystallization)	Literature
CH_3	$C_5H_8O_4$	110–111° (water)	[5]
C_2H_5	$C_6H_{10}O_4$	96–97 (chloroform)	[6,7]
n.-C_3H_7	$C_7H_{12}O_4$	[illegible] (benzene)	[5]
iso-C_3H_7	$C_7H_{12}O_4$	116.5–117 (alcohol)	[3,5]

TABLE 4. Diethyl Esters of Alkylsuccinic Acids

R CH(COOC$_2$H$_5$)—CH$_2$(COOC$_2$H$_5$) (V)

R	Empirical formula	Boiling point (pressure in mm)	Yield (%)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Literature
CH_3	$C_9H_{16}O_4$	102° (15)	78.4	1.0244	1.4231	46.79	47.07	[5, 8]
C_2H_5	$C_{10}H_{18}O_4$	117 (17)	77.6	0.9992	1.4240	51.65	51.69	[6, 7]
n.-C_3H_7	$C_{11}H_{20}O_4$	107 (9)	78.2	—	—	—	—	[5]
iso-C_3H_7	$C_{11}H_{20}O_4$	114 (7)	87.5	0.9970	1.4296	55.99	56.31	[5]

4. Esters of alkylsuccinic acids (V). Diethyl ester of ethylsuccinic acid (V, R = C_2H_5). Prepared from 260 g of ethylsuccinic acid (IV, R = C_2H_5) by boiling with 1040 ml of absolute alcohol in presence of 20.8 ml of concentrated sulfuric acid. Yield 279 g (77.6%). The diethyl esters of methyl- (V, R = CH_3), propyl- (V, R = n-C_3H_7) and isopropyl- (V, R = iso-C_3H_7) succinic acids were prepared by the same procedure (Table 4).

5. Esters of α-alkyl-α'-formylsuccinic acids (VI). Diethyl ester of α-ethyl-α'-formylsuccinic acid (VI, R = C_2H_5). To a suspension of 93.3 g of sodium methoxide in 650 ml of anhydrous toluene were added 279 g of diethyl ester of ethylsuccinic acid (V, R = C_2H_5) and 166 g of ethyl formate. The suspension of sodium methoxide was prepared by addition of 10% excess of absolute methanol to finely shredded sodium in toluene; after formation of the sodium methoxide, the excess methanol was distilled off in the form of its azeotrope with toluene. The reaction mixture was stood for two days at 10-15°. Addition was then made of 426 ml of iced water and the toluene layer was separated, the toluene distilled off and the residue distilled in vacuo to give 85 g of unchanged ethylsuccinic ester (V, R = C_2H_5). The aqueous layer was neutralized with the calculated quantity of 20% sulfuric acid (test with Congo). The resulting oily product was separated, the aqueous layer extracted with toluene (twice with 100 ml each) and the extracts added to the main bulk. The solvent was taken off in vacuo (10-15 mm). Formylethylsuccinic ester was obtained and employed for reduction without purification. Yield 199.2 g (90.2% allowing for the ethylsuccinic ester recovered).

Ethyl esters of α-methyl- (VI, R = CH_3), α-propyl- (VI, R = n-C_3H_7) and α-isopropyl- (VI, R = iso-C_3H_7) α'-formylsuccinic acids were prepared by the same procedure (Table 5).

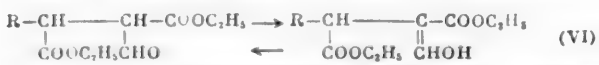
6. Esters of α-alkyl-γ-butyrolactone-β-carboxylic acids (VII, R' = C_2H_5). Ethyl esters of racemic stereoisomeric α-ethylparaconic acids (VII and VIIa, R = R' = C_2H_5). Reduction of 199.2 g of technical formylethylsuccinic ester (VI, R = C_2H_5) was performed in a stainless steel, rotating autoclave in presence of 20 g of skeletal nickel catalyst and 200 ml of anhydrous alcohol at an initial pressure of 80-100 atm and 110-120° for 3-4 hr. After completion of reduction, the catalyst was separated, the solvent distilled off and the residue distilled in vacuo (10 mm) to give approximately three equal fractions: 1st, to 140°; 2nd, 140-144°; 3rd, 145-148°. These were cooled to -15 to -12° and the crystals were separated. The filtrate was redistilled and frozen. There were obtained about 80 g of liquid, stable α-ethylparaconic ester and 76 g of crystalline, labile α-ethylparaconic ester. Total yield of ethylparaconic esters 156 g (96.8%). The labile α-ethylparaconic ester was recrystallized from toluene and, for preparation of analytically pure substance, from ether.

Ethyl esters of methyl- (VII and VIIa, R = CH_3, R' = C_2H_5), propyl- (VII and VIIa, R = n-C_3H_7, R' = C_2H_5) and isopropyl- (VII and VIIa, R = iso-C_3H_7, R' = C_2H_5) paraconic acids were similarly prepared.

7. α-Alkyl-γ-butyrolactone-β-carboxylic acids (VII and VIIa, R' = H). Racemic stereoisomeric ethylparaconic acids. A mixture of 50 g of crystalline, labile ethylparaconic ester (VII, R = R' = C_2H_5) and 177 ml of 10% hydrochloric acid was boiled for 4 hr. The solution was then evaporated to dryness in vacuo. The residue was dried and then twice recrystallized from 160 ml of anhydrous toluene. Yield 40 g (79.8%).

More prolonged heating is required for hydrolysis of the stable form (8-10 hr).

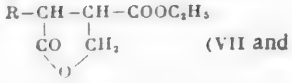
TABLE 5. Diethyl Esters of α-Alkyl-α'-formylsuccinic Acids



(VI)

R	Empirical formula	Boiling point (pressure in mm)	Yield (in %)	d_4^{20}	n_D^{20}	Found			Calculated			Literature
						MR_D	% C	% H	MR_D	% C	% H	
CH_3	$C_{10}H_{16}O_5$	121—127° (9)	86.7	1.1140	1.4530	52.46	55.55	7.69	51.70, 52.75	55.54	7.45	[9]
C_2H_5	$C_{11}H_{18}O_5$	117—119 (7)	90.2	1.0860	1.4496	56.93	57.38	7.83	56.32, 57.36	57.36	7.87	[10]
n-C_3H_7	$C_{12}H_{20}O_5$	167— 72 (15)	86.1	1.0677	1.4490	61.35	59.19	8.39	60.93, 61.98	59.00	8.25	—
iso-C_3H_7	$C_{12}H_{20}O_5$	141—147 (6)	79.1	1.0561	1.4512	62.30	58.71	8.02	60.93, 61.98	59.00	8.25	[11]

TABLE 6. Ethyl Esters of α-Alkylparaconic Acids

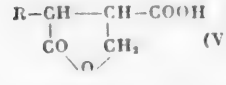


(VII and VIIa, $R' = C_2H_5$)

R	Empirical formula	Boiling point (pressure in mm)	Melting point	d_4^{20}	n_D^{20}	Found			Calculated			Literature
						MR_D	% C	% H	MR_D	% C	% H	
CH_3 stable	$C_8H_{12}O_4$	138—140° (11)	—	1.1470	1.4486	40.23	55.88	7.33	40.25	55.81	7.02	[9]
CH_3 labile	$C_8H_{12}O_4$	148—150 (11)	—	1.1545	1.4511	40.16	55.88	7.35	40.25	55.81	7.02	—
C_2H_5 stable	$C_9H_{14}O_4$	140—141 (10)	—	1.1076	1.4475	44.96	58.13	7.48	44.87	58.02	7.57	[10]
C_2H_5 labile	$C_9H_{14}O_4$	148 (10)	48—49°	—	—	—	57.99	7.67	—	58.02	7.57	[10]
n-C_3H_7 stable	$C_{10}H_{16}O_4$	143—145 (10)	—	—	—	—	60.23	8.25	—	59.98	8.05	—
n-C_3H_7 labile	$C_{10}H_{16}O_4$	150—151 (10)	52—53	—	—	—	60.06	8.30	—	59.98	8.05	—
iso-C_3H_7 stable	$C_{10}H_{16}O_4$	148—150 (8)	—	1.0832	1.4478	49.46	60.10	8.19	49.49	59.98	8.05	[11]
iso-C_3H_7 labile	$C_{10}H_{16}O_4$	154—155 (8)	54—55	—	—	—	60.18	8.32	—	59.98	8.05	[11]

Racemic stereoisomeric methyl- (VII and VIIa, R = CH_3, R' = H), propyl- (VII and VIIa, R = n-C_3H_7, R' = H) and isopropyl- (VII and VIIa, R = iso-C_3H_7, R' = H) paraconic acids were prepared by the same procedure.

TABLE 7. α-Alkylparaconic acids.



(VII, VIIa, R' = H)

R	Empirical formula	Melting point	Melting point of mixed specimen	Yield (in %)	Found % C	Found % H	Calc. % C	Calc. % H	Literature
CH_3 stable	$C_6H_8O_4$	94–94.5° (butanol)	79–80.5°	52.1	49.95	5.50	50.00	5.59	[9]
CH_3 labile		128.5–130 (butanol)		58.3	49.69	5.83			–
C_2H_5 stable	$C_7H_{10}O_4$	87.5–88 (ethanol)	64–67	70.0	53.20	6.38	53.16	6.37	[10,12]
C_2H_5 labile		89–90 (toluene)		79.6	53.38	6.23			[10]
n-C_3H_7 stable	$C_8H_{12}O_4$	82–83 (benzene)	69–72	70.3	55.99	7.08	55.81	7.02	–
n-C_3H_7 labile		155–156 (benzene)		81.1	55.86	6.60			–
iso-C_3H_7 stable	$C_8H_{12}O_4$	94–95 (benzene)	76–78	68.0	55.73	6.92	55.81	7.02	[11]
iso-C_3H_7 labile		161–162 (water)		69.7	55.90	6.86			[11]

SUMMARY

1. Racemic stereoisomeric α-methyl-, α-ethyl-, α-propyl- and α-isopropylparaconic acids were synthesized.

2. The racemic stereoisomeric forms of α-alkylparaconic esters, prepared by reduction of α-alkyl-α'-formylsuccinic esters with hydrogen in presence of Raney nickel, were isolated.

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SYNTHESIS OF OPTICALLY ACTIVE α-ALKYL-γ-BUTYROLACTONE-β-CARBOXYLIC (α-ALKYLPARACONIC) ACIDS

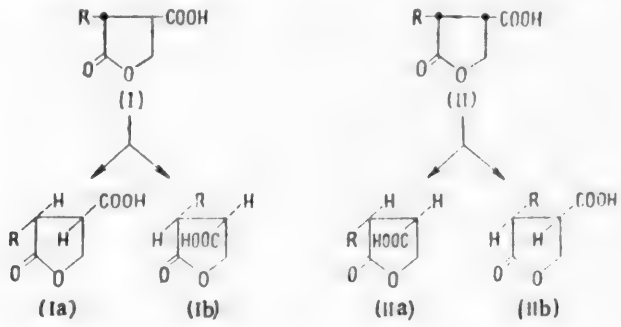
M. E. Maurit, R. P. Shternberg, A. M. Pakhomov, G. I. Basilevskaya, G. V. Smirnova, and N. A. Preobrazhenskii

Moscow Institute of Fine Chemical Technology

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp.2256-2259, July, 1960
Original article submitted June 29, 1959

In the preceding communication we described the synthesis and properties of α-alkylparaconic acids [1]. According to structural theory, two racemic steroisomeric forms and a corresponding number of optically active forms are possible for α-alkyl-γ-butyrolactone-β-carboxylic (α-alkylparaconic) acids.

In the present paper we describe methods of resolving the stereoisomeric racemic α-alkyl-γ-butyrolactone-β-carboxylic acids (I and II) into the optical antipodes [2] (Ia, Ib and IIa, IIb).



EXPERIMENTAL

I. Resolution of stable racemic α-alkylparaconic acids (I) into the optical antipodes (Ia and Ib). a) Strychnine salts of stable levo and dextro α-isopropylparaconic acids.

To a solution of 5 g of stable, racemic α-isopropylparaconic acid (I, R = iso-C_3H_7, m.p. 94-95°) in 12 ml of water at 80° was added 9.7 g of strychnine. After 2-hours' heating at 80°, the solution was left overnight in a refrigerator. The deposited crystals were separated and recrystallized from 15 ml of water. Yield of strychnine salt of the levo acid 5.7 g (77.5%).

The filtrate from the strychnine salt of the levo form of α-isopropylparaconic acid was concentrated at 30-40° and 10 mm to 1/3 of its original volume. After cooling, the crystals were separated and the filtrate evaporated to dryness in vacuo. The residue was dried by addition of anhydrous alcohol and subsequent distillation of the latter in vacuo. To the resulting glassy mass was added 5 ml of anhydrous alcohol. The resulting crystals were collected and recrystallized three times from alcohol. Yield of strychnine salt of dextro acid 5.2 g (70.7%).

Stable levorotatory and dextrorotatory α-isopropylparaconic acids (Ia and Ib, R = iso-C_3H_7). To a cooled saturated solution of 5.7 g of strychnine salt of stable levo α-isopropylparaconic acid in 114 ml of water was

added (with cooling) the calculated quantity of 0.2 N potassium hydroxide solution. The precipitated strychnine was separated and the strychnine residues in the filtrate extracted with ether. The solution was then neutralized with 5% hydrochloric acid and evaporated to dryness in vacuo. The levo α-isopropylparaconic acid was extracted from the dry residue with ether. The solvent was distilled off and the acid twice recrystallized from 2 ml of water. Yield 1.62 g (83.6%). M.p. 89-90°, $[\alpha]_D^{18}$ - 48.5° (water, c 3.650).

Found %: C 55.85; H 6.73. $C_8H_{12}O_4$. Calculated %: C 55.81; H 7.02

The dextro acid was isolated by the same method from 10 g of the strychnine salt of the stable dextro form of α-isopropylparaconic acid. Yield 3.17 g (93.2%). M.p. 89-89.7° (from benzene), $[\alpha]_D^{19}$ + 46.3° (water, c 3.00).

Found %: C 55.78; H 7.07. $C_8H_{12}O_4$. Calculated %: C 55.81; H 7.02.

Strychnine salts of stable levo and dextro α-ethylparaconic acids. Reaction of 26.9 g of stable racemic α-ethylparaconic acid (I, R = C_2H_5, m.p. 87.5-88°) with 53.46 g of strychnine in 55 ml of water by the procedure described for the strychnine salts of optically active stable α-isopropylparaconic acids gave 39.5 g of the salt of stable levo α-ethylparaconic acid which was recrystallized twice from 20 and 18 ml of water respectively. Yield 32.8 g (78.3%).

From the filtrate was isolated the strychnine salt of the dextro acid which was recrystallized from anhydrous alcohol. Yield 26.9 g (64.2%).

Stable levorotatory and dextrorotatory α-ethylparaconic acids (Ia and Ib, R = C_2H_5). Levo α-ethylparaconic acid was prepared from 32.8 g of strychnine salt of stable levo α-ethylparaconic acid dissolved in 636 ml of water. Yield 8.5 g (80.5%). Colorless crystals, readily soluble in alcohol, ether, chloroform and hot water, less soluble in cold water. M.p. 105-105.5° (from water), $[\alpha]_D^{20}$ -58.3° (water, c 3.8835).

Found %: C 53.20; H 6.47. $C_7H_{10}O_4$. Calculated %: C 53.16; H 6.37.

The dextro acid was isolated from 26.9 g of strychnine salt of stable dextro α-ethylparaconic acid dissolved in 80 ml of water. Yield 7.8 g (90.3%). Colorless, silky plates. M.p. 104.5-105.5° (from alcohol), $[\alpha]_D^{20}$ + 58.55° (water, c 3.9126).

Found %: C 53.26; H 6.55. $C_7H_{10}O_4$. Calculated %: C 53.16; H 6.37.

II. Cleavage of labile racemic α-alkylparaconic acids (II) into the optical antipodes (IIa and IIb). Brucine salts of labile dextro and levo α-methylparaconic acids.

To a solution of 2.2 g of labile racemic α-methylparaconic acid (II, R = CH_3, m.p. 125-126°) in 12 ml of water was added 6 g of brucine, and the reaction mixture was heated for an hour at 50-55°. After cooling, the precipitate was separated and recrystallized three times from three times the quantity of water. Yield of brucine salt of labile dextro α-methylparaconic acid 2.7 g (65.7%). M.p. 118-123°, $[\alpha]_D^{20}$ -20.7° (chloroform, c 2.548). The filtrate from the brucine salt of the dextro acid was evaporated in vacuo to 1/3 of its original volume, the precipitate was separated and the filtrate from the latter evaporated to dryness at 35-40° and 10 mm. The dry residue was washed with acetone twice (10 ml each time). Yield of brucine salt of labile levo α-methylparaconic acid 3 g (72.9%). M.p. 137-140°, $[\alpha]_D^{20}$ -31.8° (chloroform, c 10.944).

Labile dextrorotatory and levorotatory α-methylparaconic acids (IIa and IIb, R = CH_3). The labile optically active α-methylparaconic acids were obtained from their brucine salts by the procedure described for isolation of stable levo α-isopropylparaconic acid. From 2.4 g of brucine salt of labile dextro α-methylparaconic acid was obtained the dextro acid in a yield of 0.45 g (70.1%). M.p. 123-124° (from benzene), $[\alpha]_D^{20}$ + 19.7° (water, c 9.908).

Found %: C 50.03; H 5.63. $C_6H_8O_4$. Calculated %: C 50.00; H 5.59.

The levo acid was isolated from 2.5 g of brucine salt of labile levo α-methylparaconic acid. Yield 0.5 g (64.7%). M.p. 122.5-124°, $[\alpha]_D^{20}$ - 19.15° (water, c 10.188).

Found %: C 49.90; H 5.38. $C_6H_8O_4$. Calculated %: 50.00; H 5.59.

A mixture of 0.02 g each of labile dextrorotatory and levorotatory α-methylparaconic acids melted at 129-130°.

Brucine salts of dextro and levo α-ethylparaconic acids. Reaction of 30 g of labile racemic α-ethylparaconic acid (II, R = C_2H_5, m.p. 89-90°), dissolved in 150 ml of water, with 73.5 g of brucine gave 50.8 g of the brucine salt of the dextro acid. Yield 96.9%. M.p. 99-102°. Colorless, small needles, poorly soluble in cold water, readily in hot water and acetone.

The filtrate was evaporated in vacuo and the dry residue washed with acetone (two lots of 50 ml each). The brucine salt of the levo acid was obtained with m.p. 105-107°. Acicular crystals, readily soluble in water, poorly in acetone. Yield 39.2 g (74.8%).

Labile dextrorotatory and levorotatory α-ethylparaconic acid (IIa and IIb, R = C_2H_5). From 50.8 g of brucine salt of labile dextro α-ethylparaconic acid, dissolved in 660 ml of water, was isolated the dextro acid in a yield of 10 g (68.7%). Colorless crystals, readily soluble in water, hot ether and benzene, poorly soluble in cold benzene. M.p. 121-122°, $[\alpha]_D^{20}$ + 53.55° (water, c 4.426).

Found %: C 53.32; H 6.43. $C_7H_{10}O_4$. Calculated %: C 53.16; H 6.37.

From 39.2 g of brucine salt of labile levo α-ethylparaconic acid was obtained 8.1 g of levo acid. Yield 72.2%. Colorless needles, readily soluble in hot ether and benzene, less soluble in cold benzene and water. M.p. 120-120.5°, $[\alpha]_D^{20}$ -53.75° (water, c 3.915).

Found %: C 53.02; H 6.39. $C_7H_{10}O_4$. Calculated %: C 53.16; H 6.37.

SUMMARY

1. Racemic α-alkylparaconic acids of the stable form were resolved with the help of strychnine, and the racemic acids of the labile form were resolved with the help of brucine.

2. The stable optically active α-isopropyl- and α-ethylparaconic acids and the labile α-methyl- and α-ethylparaconic acids were obtained.

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SYNTHESIS OF THE ETHYL ESTER OF 4,6,9,11,14-PENTAKETOPENTADECANOIC ACID AND THE ETHYL ESTER OF 4,6,9,11,14,16,19-HEPTAKETOEICOSANOIC ACID

N. V. Zotchik, R. P. Evstigneeva, and N. A. Preobrazhenskii

Moscow Institute of Fine Chemical Technology

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2259-2261,
July, 1960
Original article submitted June 29, 1959

In the course of further investigation of the Claisen condensation of the ethyl ester of levulinic acid (I) [1] and the ethyl ester of 4,6,9-triketocapric acid (II), we prepared the ethyl ester of 4,6,9,11,14-pentaketopentadecanoic acid (III, R = C_2H_5) and acid (III, R = H) and the ethyl ester of 4,6,9,11,14,16,19-heptaketoeicosanoic acid (IV). A secondary product in the former case is ester (II).

$$\underset{(I)}{CH_3COCH_2CH_2COOC_2H_5} \longrightarrow \underset{(II)}{CH_3COCH_2CH_2COCH_2COCH_2CH_2COOC_2H_5} +$$

$$+ \underset{(III)}{CH_3COCH_2CH_2COCH_2COCH_2CH_2COCH_2COCH_2CH_2COOR}$$

$$(II) \longrightarrow \underset{(IV)}{CH_3COCH_2CH_2COCH_2COCH_2CH_2COCH_2COCH_2CH_2COCH_2COCH_2CH_2COOC_2H_5}$$

The esters were separated and purified via the copper enolates [2]. As β-diketones, the prepared compounds give a deep red color with alcoholic ferric chloride; they titrate with caustic alkali and readily form copper derivatives. The infrared absorption spectrum of the copper complexes exhibits a considerable increase in intensity in the 1625-1615 cm^{-1} region (enolic structure) in comparison with the spectrum of the ester. This is accounted for by the chelate structure of the copper enolates. The band intensity at 1720 cm^{-1}, characterizing free keto groups [3], is correspondingly weakened.

Results of determination of the number of methyl groups [4] attached to carbon (two groups) confirm the linear structure of the esters obtained.

EXPERIMENTAL

Ethyl ester of 4,6,9,11,14-pentaketopentadecanoic acid (III). To 5.65 g of sodium wire in 100 ml of absolute ether was added 35.3 g of ethyl levulinate. Reaction proceeded at room temperature and was completed in 5-6 hr. The sodium enolate was separated, washed with 20 ml of absolute ether and dissolved in 450 ml of iced water. The solution was acidified with 60 ml of dilute (1:1) hydrochloric acid. An oily product separated out and was extracted three times with ether (100 ml each) and dried with sodium sulfate. The solvent was removed in vacuo and the residue (14 g) dissolved in 250 ml of methyl alcohol to which was then added 100 ml of saturated copper acetate solution. The copper enolate was separated and washed with 20 ml of methyl alcohol and 20 ml of ether. Yield 7.5 g. The copper enolate was suspended in 30 ml of anhydrous methyl alcohol and treated with hydrogen sulfide. The precipitated copper sulfide was filtered off and washed with 10 ml of absolute methanol. The solvent was removed in vacuo. The ethyl ester of 4,6,9,11,14-pentaketopentadecanoic acid was isolated as a viscous, yellow liquid. Yield 4.75 g (17.08%). MR_D 83.80; calcd. 82.41 (for the keto form), 84.50 (for the enol form).

Found %: C 59.86, 59.87; H 7.15, 7.83; enol form 99.4; CH_3 (Kuhn and Roth method) 5.36. $C_{17}H_{24}O_7$. Calculated %: C 60.00, H 7.10; CH_3 (for two groups) 8.82

The methanolic mother liquor from the copper enolate was evaporated in vacuo and the residue treated with 50 ml of ether. Copper enolate solidified and was filtered, washed with 20 ml of anhydrous ether and dried in the air. Yield 8.3 g. The copper enolate was decomposed with hydrogen sulfide. The residue was a viscous, reddish-yellow liquid – 4,6,9,11,14-pentaketopentadecanoic acid. Yield 4.7 g (18.4%).

Found %: C 58.03; H 6.50. $C_{15}H_{20}O_7$. Calculated %: C 57.69; H 6.42.

After removal of the solvent, the ethereal mother liquor deposited 2.1 g of oily substance – the ethyl ester of 4,6,9-triketocapric acid.

Ethyl ester of 4,6,9,11,14,16,19-heptaketoeicosanoic acid (IV). To 1.9 g of finely shredded sodium in 50 ml of anhydrous xylene was added 10 g of ethyl ester of 4,6,9-triketocapric acid, and the mixture refluxed for 5-6 hr. The next morning the sodium enolate was separated, washed with 20 ml of anhydrous ether and dried in the air. Yield 12.1 g. The enolate was dissolved in 100 ml of iced water, and the cloudy solution was extracted twice with ether (20 ml each time) and acidified with 20 ml of dilute (1:1) hydrochloric acid. The oily product was extracted with ether (3 times with 50 ml each) and dried with sodium sulfate. Removal of solvent in vacuo left 4.8 g of very viscous, brownish-red oil. In the same manner as in the preceding experiment, 2.7 g of copper enolate was isolated. The methanolic mother liquor, after trituration with ether, gave 1.9 g of copper enolate. The enolates were decomposed with hydrogen sulfide. The ethyl ester of 4,6,9,11,14,16,19-heptaketoeicosanoic acid was obtained. Yield 1.5 g (16.5%). An amorphous, brownish-yellow substance. MR_D 109.00; calcd. 105.52 (for the keto form), 108.7 (for the enol form).

Found %: C 60.14; 60.30; H 6.73, 6.82; enol form 98.50; CH_3 (Kuhn–Roth method) 4.38. $C_{22}H_{30}O_9$. Calculated %: C 60.27; H 6.90; CH_3 (for two groups) 6.85.

Subsequently an additional 1.00 g (11.04%) of ethyl ester of 4,6,9,11,14,16,19-heptaketoeicosanoic acid was isolated.

Found %: C 60.00; H 6.73; enol form 81.00. $C_{22}H_{30}O_9$. Calculated %: C 60.27; H 6.90.

From the ethereal mother liquor was isolated 0.8 g of the ethyl ester of 4,6,9-triketocapric acid.

SUMMARY

Ethyl esters of 4,6,9,11,14-pentaketopentadecanoic acid and of 4,6,9,11,14,16,19-heptaketoeicosanoic acid were synthesized.

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CLAISEN CONDENSATION OF ESTERS OF β-METHYLLEVULINIC ACID

R. P. Evstigneeva, V. A. Glybina, E. V. Okart,

and N. A. Preobrazhenskii

Moscow Institute of Fine Chemical Technology

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2261-2263,
July, 1960
Original article submitted June 29, 1959

In continuation of our work on the ester-condensation of esters of levulinic acid [1], we investigated esters of β-methyllevulinic acid.

β-Methyllevulinic acid and its esters were prepared by the reactions:

$$CH_3COCH(CH_3)-Br + NaCH(COOC_2H_5)_2 \rightarrow$$

$$\rightarrow CH_3COCH(CH_3)CH(COOC_2H_5)_2 \rightarrow CH_3COCH(CH_3)CH_2COOR$$

(I) (II)

Condensation of α-bromoethyl methyl ketone [2] with sodium malonic ester gave the ethyl ester of α-carbethoxy-β-methyllevulinic acid [3] (I). Saponification of compound (I) followed by decarboxylation gave β-methyllevulinic acid (II, R = H). Esterification of the acid gave the corresponding esters (II, R = CH_3 and C_2H_5). Ethyl β-methyllevulinate (II, R = C_2H_5) can be prepared directly from (I) by selective saponification of one of the carbethoxyl groups and subsequent decarboxylation. Condensation of the ethyl or methyl ester of β-methyllevulinic acid led to the corresponding esters of 3,8-dimethyl-4,6,9-triketocapric acid (III).

$$CH_3COCH(CH_3)CH_2COCH_2COCH(CH_3)CH_2COOR$$

(III)

Condensation between the ethyl (II, R = C_2H_5) and methyl (II, R = CH_3) esters of β-methyllevulinic acid takes place with formation of the methyl ester of 3,8-dimethyl-4,6,9-triketocapric acid (III, R = CH_3). The linear structure of the resulting products of condensation was confirmed by Kuhn–Roth oxidation. Saponification of esters of 3,8-dimethyl-4,6,9-triketocapric acid leads to the corresponding acid (III, R = H) which gives a monosemicarbazone. In this last respect the acid resembles unsubstituted 4,6,9-triketocapric acid [1].

EXPERIMENTAL

Ethyl β-methyllevulinate (II, R = C_2H_5). To the sodium ethoxide prepared from 4 g of sodium and 100 ml of anhydrous alcohol were added 40 g of ethyl ester of α-carbethoxy-β-methyllevulinic acid (b.p. 118-120° at 3 mm) and 3 ml of water. The reaction mixture was stood overnight and then heated for an hour. The excess alcohol was taken off in vacuo; the residue was dissolved in 100 ml of water and unreacted dicarboxylic ester

extracted with ether. The aqueous solution was acidified with hydrochloric acid (to Congo) and extracted with 200 ml of ether. The solvent was removed from the dried solution and the residue heated at 150-160° for 3 hr and then distilled.

1st fraction: ethyl β-methyllevulinate; yield 10.1 g. B.p. 99-100° (14 mm).

2nd fraction: β-methyllevulinic acid; yield 4.9 g. B.p. 115-116° (3 mm). Total yield of ester and acid 68.1% allowing for the ester recovered (5.5 g).

Ethyl ester of 3,8-dimethyl-4,6,9-triketocapric acid (III, R = C_2H_5). To 1.68 g of sodium wire in 100 ml of dry ether was added portionwise 23 g of ethyl β-methyllevulinate. The next day the ether was decanted and the salt precipitate washed with ether, dissolved in iced water, acidified with hydrochloric acid (to Congo) and extracted with ether. The product was dried with sodium sulfate, the solvent removed and the residue distilled. Yield 5.2 g (30.6%) allowing for the recovered ethyl ester of β-methyllevulinic acid (3.0 g).

B.p. 160-162° (0.35 mm), d_4^{20} 1.1180, n_D^{20} 1.4870; MR_D 69.18; Calc. 68.54 (for keto form), 69.39 (for enol form).

Found %: C 62.16, 62.21; H 7.88, 8.38; enol form (titration with alkali) 34; CH_3 (Kuhn–Roth) 14.8. M 273 (cryoscopic measurement in dibromoethane). $C_{14}H_{22}O_5$. Calculated %: C 62.22; H 8.15; CH_3 22.1 (for four CH_3 groups). M 270.

3,8-Dimethyl-4,6,9-triketocapric acid (III, R = H). To a solution of 1 g of ester of 3,8-dimethyl-4,6,9-triketocapric acid in 2.5 ml of methyl alcohol was added 20 ml of dilute (1:2) hydrochloric acid. The mixture was refluxed for 24 hr. The hot hydrolyzate was treated with 0.2 g of active carbon and filtered. The acid separated in the form of a viscous, oily liquid insoluble in ether. Yield 0.4 g (50%). The monosemicarbazone of the acid was isolated from the methyl alcohol in the form of colorless crystals with m.p. 180-181°.

Found %: C 52.6; H 7.14; N 14.11. Equiv. 242.3. $C_{13}H_{21}O_5N_3$. Calculated %: C 52.2; H 7.02; N 14.05. Equiv. 242

Methyl ester of 3,8-dimethyl-4,6,9-triketocapric acid (III, R = CH_3). From 7 g of methyl β-methyllevulinate and 0.56 g of sodium in 100 ml of absolute ether, under conditions similar to those described above, was obtained 2.3 g of methyl ester of 3,8-dimethyl-4,6,9-triketocapric acid. Yield 37.5%.

B.p. 174-176° (0.5 mm), MR_D 64.73; calc. 63.9 (for keto form), 64.9 (for enol form).

Found %: C 60.75, 60.99; H 7.95; 8.06; enol form (titration with alkali) 38; CH_3 (by Kuhn–Roth method) 11.5. M 246. $C_{13}H_{20}O_5$. Calculated %: C 60.92; H 7.87; CH_3 17.6 (for three CH_3 groups). M 256.

From 4 g of ethyl and methyl esters of β-methyllevulinic acid, under the same conditions, was obtained 2 g (30.4%) of methyl ester of 3,8-dimethyl-4,6,9-triketocapric acid with b.p. 174-176° (0.5 mm).

Found %: C 61.16; H 7.80. $C_{13}H_{20}O_5$. Calculated %: C 60.92; H 7.87.

SUMMARY

The methyl and ethyl esters of 3,8-dimethyl-4,6,9-triketocapric acid were synthesized and their structure confirmed.

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INVESTIGATIONS OF AMINES AND AMMONIUM COMPOUNDS

XII. SYNTHESIS OF SOME AMINES

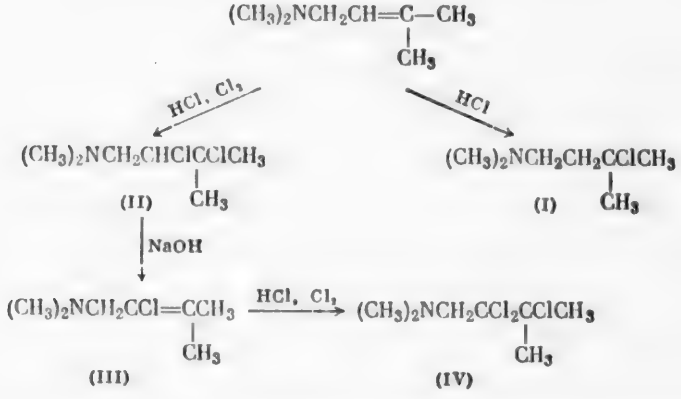
A. T. Babayan, G. T. Martirosyan, N. G. Vartanyan, and M. G. Indzhikyan

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp 2263-2267,
July, 1960
Original article submitted May 22, 1959

The present paper is concerned with the synthesis of a series of unsaturated and chlorine-containing amines: 1-dimethylamino-3-chloro-3-methylbutane (I), 1-dimethylamino-2,3-dichloro-3-methylbutane (II), 1-dimethylamino-2-chloro-3-methyl-2-butene (III), 1-dimethylamino-2,2,3-trichloro-3-methylbutane (IV), β-hydroxyethyl-(3-chlorobuten-2-yl)amine (V), β-hydroxyethyl-di-(3-chlorobuten-2-yl)amine (VI), β-hydroxyethylbutyn-2-ylamine (VII), β-hydroxyethyl-di-(butyn-2-yl)amine (VIII), methylphenyl-(3-chlorobuten-2-yl)amine (IX), methylphenylallylamine (X), methylphenyl-γ,γ-dimethylallylamine (XI), benzylallylamine (XII), benzyldiallylamine (XIII), benzylphenylallylamine (XIV) and methyldibenzylamine (XV).

The first four amines were synthesized from 1-dimethylamino-3-methyl-2-butene by the following reactions:



Investigation of the chlorination of 1-dimethylamino-3-chloro-2-butene hydrochloride previously showed that the presence of an ammonium group inhibits the L'vov reaction and leads to products of addition of chlorine at the double bond [1]. Similarly the chlorination of 1-dimethylamino-3-methyl-2-butene and of amine (III) proceeds smoothly. Hydrochlorination of 1-dimethylamino-3-methyl-2-butene proceeds under the same conditions as hydrochlorination of trimethylethylene. Consequently, the presence of an ammonium group does not appreciably influence the character of the reaction.

As had been expected, the dehydrochlorination of amine (II) takes place with very great facility even at room temperature.

Yields, physical constants and melting points of derivatives of amines (I-IV) are set forth in Table 1.

Amines (V) and (VI) were obtained by reaction of 1,3-dichloro-2-butene with ethanolamine.

TABLE 1. Physical Constants and Analyses of Amines (I-IV)

Compound	Yield in %	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Melting point of derivatives: picrate	hydrochloride	methiodide	N content of amine %: formula	calculated	found	I content of methiodide (%): calculated	found
I	86.1	39–40°(7)	0.8883	1.4340	43.80	43.33	169–170°	161.5°	173°	$C_7H_{16}NCl$	9.40	9.63	–	–
II	85.2	72–73(10)	1.0487	1.4632	48.03	48.20	156	196	223	$C_7H_{15}NCl_2$	7.60	7.68	38.96	38.98
III	79.0	64–65(20)	0.9403	1.4600	42.91	42.87	148	200	214	$C_7H_{14}NCl$	–	–	43.86	43.97
IV	80.5	73–74(3)	1.1730	1.4820	53.10	53.07	186	215	185	$C_7H_{14}NCl_3$	6.40	6.31	35.23	35.36

TABLE 2. Yields of Amines (V) and (VI) in Dependence on the Molar Ratio of Reactants

Molar ratio of 1,3-dichloro-2-butene to ethanolamine	Yield (%) (V)	Yield (%) (VI)	Total yield (%)
1:3	53.8	23.5	77.3
1:2	41.5	38.4	79.9
1:15	14.5	66.0	80.5

$$H_2NCH_2CH_2OH \xrightarrow{CH_3CCl=CHCH_2Cl} \begin{cases} HOCH_2CH_2NHCH_2CH{=}CCl{-}CH_3 \ (V) \\ HOCH_2CH_2N(CH_2CH{=}CCl{-}CH_3)_2 \ (VI) \end{cases}$$

Yields of amines (V) and (VI) depend on the ratio of 1,3-dichloro-2-butene to ethanolamine (Table 2).

Our earlier method of preparing tertiary amines with a butyl radical [2] was employed in the synthesis of amine (VIII). Reaction between 1,3-dichloro-2-butene and compound (VI) gave β-hydroxyethyl-tri-(3-chlorobuten-2-yl)ammonium chloride whose alkaline cleavage led to compound (VIII).

$$CH_3CCl{=}CHCH_2Cl + (VI) \longrightarrow [HOCH_2CH_2N(CH_2CH{=}CClCH_3)]_3{}^+Cl^- \xrightarrow{NaOH} \longrightarrow HOCH_2CH_2N(CH_2C{\equiv}C{-}CH_3)_2 \ (VIII)$$

Dehydrochlorination of (V) to (VII) was effected by heating with pulverized potassium hydroxide on a boiling water bath.

Data for amines (V) and (VIII) are set forth in Table 3.

Amines (IX) to (XV) were prepared by "nitralkylation" with alkyl halides in an aqueous alkaline medium in presence of catalytic quantities of quaternary ammonium salts [3]. Amines (IX) and (XI) are described for the first time and data for them are given in Table 3. Concerning the remaining amines, already described in the literature, we report only their yields: (X) and (XIV)–72%, (XII)–60%, (XIII)–66% and (XV)–54%

Amine (IX) has also been prepared by alkylation of methylaniline with trimethyl-(3-chlorobuten-2-yl) ammonium iodide in 65% yield [4].

$$C_6H_5NHCH_3 + [(CH_3)_3NCH_2CH{=}CClCH_3]^+I^- \xrightarrow{140^\circ} \longrightarrow C_6H_5N(CH_3)(CH_2CH{=}CClCH_3) + (CH_3)_3N \cdot HI \ (IX)$$

EXPERIMENTAL

1. Preparation of 1-dimethylamino-3-chloro-3-methylbutane (I). A solution of 1-dimethylamino-3-methyl-2-butene hydrochloride was saturated with hydrogen chloride and stood at room temperature. The mixture was carefully made alkaline with sodium carbonate, extracted with ether and distilled (see Table 1).

2. Preparation of products of chlorination of 1-dimethylamino-3-methyl-2-butene and amine (III). Chlorine was passed through a suspension of the hydrochlorides in carbon tetrachloride at -15° until the theoretical quantity had been absorbed. Evolution of hydrogen chloride was not observed (Table 1).

3. Preparation of 1-dimethylamino-2-chloro-3-methyl-2-butene (III). Amine (II) was dissolved in 25% alcoholic potassium hydroxide and stood overnight at room temperature. The mass was then heated for an hour at 50°. The precipitated potassium chloride was filtered off. The filtrate was diluted with water and the amine extracted with ether and distilled (Table 1).

4. Preparation of β-hydroxyethyl-3-chloro-2-butenylamines (V) and (VI). To water-cooled ethanolamine was added 1,3-dichloro-2-butene. Completion of reaction was established by treatment of a sample with hydrochloric acid. Yields of amines (V) and (VI) in dependence on the molar ratio of 1,3-dichloro-2-butene to ethanolamine are set forth in Tables 2 and 3.

TABLE 3. Physical Constants and Analyses of Amines (V)-(IX) and (XI)

Compound	Yield (in %)	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Content of Cl and N (in %) formula	calculated	found
(V)	54	120—123° (9) M.p. 54	—	—	—	—	$C_6H_{12}ONCl$	23.74*	23.37
(VI)	66	148—149 (9)	1.1350	1.5082	62.53	62.65	$C_{10}H_{17}ONCl_2$	29.79*	29.89
(VII)	84	99—100 (8)	0.9913	1.4843	32.62	32.97	$C_8H_{11}ON$	12.4**	12.61
(VIII)	85	88—90 (7)	0.9789	1.4991	49.50	49.86	$C_{10}H_{15}ON$	8.48**	8.18
(IX)	80	130—131(10)	1.0866	1.5600	57.17	57.63	$C_{11}H_{14}NCl$	7.16**	7.5
(XI)	90	102—107 (7)	0.9938	1.5510	58.18	57.51	$C_{12}H_{17}N$	8.00**	8.45

Notes. 1. One star denotes analysis for chlorine, two stars for nitrogen. 2. The hydrochloride of (VI) has m.p. 64°, the hydrochloride of (VII) has m.p. 82°. For compound (VIII) the m.p. of the picrate of the base is 314° (from the methiodide); for compounds (IX) and (X) the melting points of the picrate are 87 and 101° respectively.

5. Dehydrochlorination of β-hydroxyethyl-(3-chloro-2-butenyl)amine. A mixture of 45 g of amine and 25 g of potassium hydroxide powder was heated on a boiling water bath for 12 hr. Potassium chloride (22 g) was precipitated. There was obtained 28.5 g (84%) of dehydrochlorinated amine (VII) (Table 3).

6. Alkaline cleavage of β-hydroxyethyl-tri-(3-chloro-2-butenyl)ammonium chloride. A solution of 23.8 g of amine (VI) and 13.75 g of 1,3-dichloro-2-butene was heated on a boiling water bath. To the resulting quaternary ammonium salt was added an aqueous solution of NaOH. Cleavage was effected by heating on a boiling water bath. The separated upper layer and the ethereal extract of the lower layer were combined, dried and fractionated to give 8 g of amine (VIII) (85% yield) (Table 3). In addition 10 g of the original amine was recovered.

7. Preparation of amines (IX-XI). To a mixture of equimolar amounts of methylaniline and the appropriate alkenyl chloride, heated on a boiling water bath in presence of catalytic amounts of a quaternary ammonium salt, was added an equimolar quantity of 5 N aqueous NaOH solution with stirring in the course of 20 min. Heating and stirring were continued for another 5 min. The upper layer was then separated and acidified. Unreacted 1,3-dichloro-2-butene was extracted with ether. Ther hydrochloric acid solution was made alkaline and the separated amine dried and distilled. Yield of (X) 81-82° (3 mm); picrate m.p. 92° [5].

8. Preparation of amines (XII)-(XV). Under conditions similar to the preceding ones, alkylation of benzylamine with an equimolar quantity of allyl bromide gave amine (XII). Reaction of benzylamine with double the molar proportion of allyl bromide gave amine (XIII). Benzylallylamine (XII): yield 60%, b.p. 200° (680 mm); picrate, m.p. 100°.

Found %: N 9.99. $C_{10}H_{13}N$. Calculated %: N 9.52.

Literature [6]: b.p. 205—208° (760 mm).

Benzyldiallyamine (XIII): yield 66%, b.p. 103-105° (6 mm); picrate, m.p. 114°.

Found %: N 7.39. $C_{13}H_{17}N$. Calculated %: N 7.49

Literature [7]: b.p. 121-124° (20 mm); picrate, m.p. 114°.

Reaction of benzylphenylamine with allyl bromide gave (XIV); yield 72%, b.p. 146° (4 mm); hydrochloride, m.p. 220°.

Literature data [8]: b.p. 178° (14 mm); hydrochloride, m.p. 220-221°.

Alkylation of methylamine with double the molar proportion of benzyl chloride in presence of a quaternary ammonium salt gave (XV); yield 54%; in the absence of catalyst the yield 25%; b.p. 287-290° (680 mm); oxalate, m.p. 192°; picrate, m.p. 107°.

Literature data [9]: b.p. 299° (760 mm); picrate, m.p. 107°.

9. Preparation of (IX) by alkylation of methylaniline with trimethyl-(3-chloro-2-butenyl)ammonium iodide. A mixture of 27.55 g of trimethyl-(3-chloro-2-butenyl)ammonium iodide and 21.4 g of methylaniline was heated

for 5 hr at 145-147°. The reaction mixture was diluted with water and extracted with ether. There was obtained 12.7 g (64.9%) of methylphenyl-(3-chloro-2-butenyl)amine with b.p. 120-122° (1 mm). The aqueous layer was made alkaline and 57% of trimethylamine was recovered by absorption in acid.

SUMMARY

1. New examples confirmed the correctness of our earlier observation that the L'vov reaction is inhibited during low-temperature chlorination of hydrochlorides of amines containing a β, γ-unsaturated radical, due to the presence of an ammonium group, and that the reaction yields products of addition of chlorine at the double bond.

2. The earlier method of "nitralkylation" in an aqueous alkaline medium in presence of catalytic quantities of quaternary ammonium salts was applied to additional preparations.

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•Original Russian pagination. See C. B. translation.

INVESTIGATIONS IN THE FIELD OF ORGANIC-OXIDE CHEMISTRY

XVII. INTERACTION OF PRIMARY-SECONDARY ACETYLENIC OXIDES WITH METHYLAMINE

V. M. Al'bitskaya, E. M. Blyakhman, and A. A. Petrov

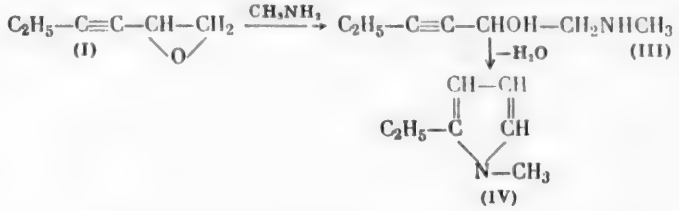
Lensovet Leningrad Technological Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2267-2269, July, 1960
Original article submitted July 16, 1959

The main regularities in the reactions of saturated α-oxides with amines and ammonia were established in the classical works of K. A. Krasuskii [1]. Peculiarities in the reactions of ethylenic α-oxides were investigated in recent years by a number of chemists, including the authors of this article [2-6]. In several works F. Ya. Perveev and co-workers investigated the interaction of ammonia and amines with acetylenic and vinylacetylenic oxides [7]. In these works it was established that, in the case of primary-tertiary and secondary-tertiary oxides, amines add to them according to K. A. Krasuskii's rule; however, the amino alcohols of the acetylene series formed in this case are more or less (depending on the structure) easily converted to homologs of pyrrole. The question of the behavior of primary-secondary acetylenic α-oxides in the given reaction remained uninvestigated.

We studied the interaction of methylamine with two acetylenic oxides of the indicated type—1,2-epoxyhexyne-3 (I) and 1,2-epoxyoctyne-3 (II).

Oxide (I) reacted with methylamine to form a mixture of amino alcohol (III) and N-methyl-2-ethylpyrrole (IV). Amino alcohol (III) gave N-methyl-2-ethylpyrrole on dehydration over KOH.



The reaction of oxide (II) with methylamine gave only N-methyl-2-butylpyrrole (V).

The formation of substituted pyrroles indicates that addition of the amine to the oxide ring takes place in strict conformity with K. A. Krasuskii's rule.

Pyrrole homologs (IV) and (V) are colorless liquids with a characteristic odor. They color a pine splinter, moistened with hydrochloric acid, red. They give a violet color with SeO_2. They form mercury derivatives and enter into the diazo coupling reaction. The infrared spectra of both substances contain bands characteristic of pyrroles in the 1300 and 1500 cm^{-1} regions [8].

Our investigation showed that primary-secondary acetylenic oxides behave the same as primary-tertiary and secondary-tertiary ones in reactions with amines.

EXPERIMENTAL

Reaction of oxide (I) with methylamine. To a fivefold excess of 33% methylamine solution, 17 g of oxide (I) was slowly (dropwise) added, the mixture being cooled and stirred [9]. The reaction mixture was kept for 4 days at room temperature and the reaction products then salted out with potash, the methylamine being simultaneously driven off. The oil formed was separated, dried with potash, and distilled in vacuo. In this case 7 g of N-methyl-2-ethylpyrrole (IV) and 3 g of high-boiling crystalline product (III) were obtained. Total yield, about 50%, reckoned on the oxide taken.

N-Methyl-2-ethylpyrrole. B.p. 58.5-59.5° (15 mm), d_4^{20} 0.9024, n_D^{20} 1.4902, MR 34.93; Calc. 35.33.

Found %: C 77.68, 77.90; H 10.32, 10.46. $C_7H_{11}N$. Calculated %: C 77.02; H 10.16.

The mercury derivative was a brownish powder with m.p. 80° (decomp.).

N-Methylaminohexyn-3-ol-2 (III). M.p. 67° (from petroleum ether).

Found %: C 66.05, 66.16; H 9.95, 10.25. $C_7H_{13}ON$. Calculated %: C 66.10; H 10.29.

Picrolonate, m.p. 111° (decomp.).

Amino alcohol (III) was dehydrated by slow distillation over solid KOH in vacuo; in this case a liquid with b.p. about 59° (15 mm) was obtained, which had all the properties of N-methyl-2-ethylpyrrc .

Reaction of oxide (II) with methylamine. Under conditions similar to those described above, 19 g of oxide (II) [9] gave 11 g (55%) of N-methyl-2-butylpyrrole (V).

N-Methyl-2-butylpyrrole. B.p. 84-85° (15 mm), d_4^{20} 0.8930, n_D^{20} 1.4745, MR 44.17; Calc. 44.56.

Found %: C 79.23, 79.48; H 10.27, 10.93. $C_9H_{15}N$. Calculated %: C 78.77; H 10.03.

Mercury derivative, m.p. 93° (decomp.).

SUMMARY

1. The reactions of 1,2-epoxyhexyne-3 with methylamine were investigated.

2. It was shown that pyrrole homologs are formed in this reaction even in the cold. In the case of the first oxide an amino alcohol—N-methylaminohexyn-3-ol-2—also was obtained; the latter was easily converted to N-methyl-2-ethylpyrrole by distillation over KOH.

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SYNTHESIS OF 2,6-DIMETHYL-Δ^1-TETRAHYDROBENZALDEHYDE ACETALS

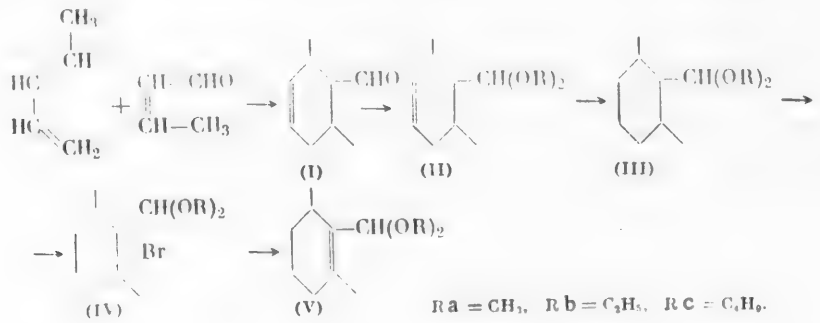
I. N. Nazarov, R. I. Kruglikova, and S. Ya. Mel'nik

Moscow Institute of Fine Chemical Technology

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2269-2274, July, 1960
Original article submitted June 1, 1959

In recent years works have appeared on the building-up of isoprenoid chains by condensation of acetals either successively with vinyl and propenyl ethers [1] or directly with 2-methylbutadienyl ether (ethoxyisoprene) [2]. In connection with this, it is of interest to synthesize acetals of aldehydes of the cyclohexene series—analogs of β-cyclocitral. These acetals may be used as starting materials for the synthesis of inadequately studied analogs of vitamin A by the above-mentioned schemes.

In the present article the preparation of 2,6-dimethyl-Δ^1-tetrahydrobenzaldehyde dimethyl, diethyl, and dibutyl acetals is described. They were synthesized according to a scheme similar to that for the preparation of the aldehyde itself [3, 4].



R a = CH_3, R b = C_2H_5, R c = C_4H_9.

The synthesis of 2,6-dimethyl-Δ^1-tetrahydrobenzaldehyde by such a scheme involves certain difficulties: the hydrogenation of aldehyde (I) does not go easily at normal pressure, and the dehydrobromination of 1-bromo-2,6-dimethylhexahydrobenzaldehyde leads to a mixture of products, difficult to resolve. Acetals of α, β-unsaturated aldehydes are obtained in low yields. The described route of synthesis, which provides for displacement of the double bond right in the acetal molecule, makes it possible to avoid these bottlenecks.

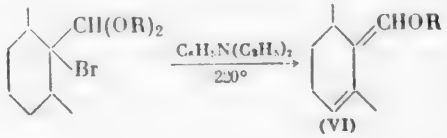
The acetalization of 2,6-dimethyl-Δ^3-tetrahydrobenzaldehyde was studied in detail in the case where its dimethyl, diethyl, and dibutyl acetals were prepared. Methyl, ethyl, and butyl alcohols, respectively, were used as acetalizing agents (in the last case water was distilled off continuously in the course of the reaction), as well as tetramethoxysilane, tetraethoxysilane, and orthoformic ester. Concentrated hydrochloric, 85% phosphoric, and

p-toluenesulfonic acids were used as catalysts. It must be noted that phosphoric acid, which is a good catalyst for preparing acetals and ketals of aliphatic and aromatic aldehydes and ketones by means of tetraalkoxysilanes [5], leads to very impure acetals in poor yields in the present case. Yields of acetals, reckoned on reacted 2,6-dimethyl-Δ^3-tetrahydrobenzaldehyde, are given in the table.

The hydrogenation of acetals (II) over a 5% $Pd/BaSO_4$ catalyst leads to the formation of the corresponding saturated acetals (III) in 95-98% yields. By the usual method for aldehydes, dibutyl acetal (IIIc) gave a 2,4-dinitrophenylhydrazone with m.p. 129-130°, which corresponds to the described 2,4-dinitrophenylhydrazone obtained from 2,6-dimethylhexahydrobenzaldehyde.

The dimethyl, diethyl, and dibutyl acetals were further brominated. In order to prevent replacement of the alkoxy group by bromine, the reaction mass was treated after bromination with an excess of the corresponding alcohol. 1-Bromo-2,6-dimethylhexahydrobenzaldehyde acetals (IV) were obtained in 60-70% yields.

α-Bromo-substituted acetals (IV) must be dehydrobrominated at a lower temperature than α-bromo-substituted aldehydes. Thus, when acetals (IVa, b, c) are briefly heated (2-3 minutes) in diethylaniline solution at 220°, dehydrobromination is accompanied by splitting-off of one of the alkoxyl groups, and the corresponding cyclic dienic ethers are formed.



(VI)

Relation Between the Yield of Acetal and the Character of the Acetalizing Agent and the Catalyst

Acetal	Acetalizing agent	Catalyst	Yield (in %)
(IIa)	$Si(OCH_3)_4$	HCl	77
(IIa)	$Si(OCH_3)_4$	H_3PO_4	13.4
(IIa)	CH_3OH	HCl	70
(IIb)	$Si(OC_2H_5)_4$	HCl	62
(IIb)	$Si(OC_2H_5)_4$	H_3PO_4	17.4
(IIb)	C_2H_5OH	HCl	59
(IIb)	$CH(OC_2H_5)_3$	p-$CH_3C_6H_4SO_3H$	90
(IIc)	C_4H_9OH	p-$CH_3C_6H_4SO_3H$	81.5

This reaction goes especially easily and completely in the case of dimethyl acetal (IVa), and with more difficulty in the case of dibutyl acetal (IVc). The alkoxydienes obtained have lower boiling points and higher refractive indices than the corresponding α, β-unsaturated acetals, and are characterized by λ_{max} 245-247 mμ (ε 23700-27500) in the UV spectrum. The 2,4-dinitrophenylhydrazone was also prepared from them by the usual method; it melted at 162.5-163.5° and corresponded to the described 2,6-dimethyl-Δ^1-tetrahydrobenzaldehyde 2,4-dinitrophenylhydrazone.

When dimethylacetal (IVa) was heated with potassium tert-butoxide in an excess of tert-butyl alcohol, 30% of the original bromo-substituted acetal (IVa) was recovered, and 30% was dehydrobrominated. Good results with regard to dehydrobromination were obtained by heating acetals (IV) with a ninefold excess of powdered KOH without solvent at 110-130°. α, β-Unsaturated acetals (V) are obtained in 55-70% yields, and are quite pure after two distillations. The 2,4-dinitrophenylhydrazone obtained from them corresponds to 2,6-dimethyl-Δ^1-tetrahydrobenzaldehyde 2,4-dinitrophenylhydrazone, melts at 162.5-163.5° [3], and has a characteristic UV absorption spectrum with λ_{max} 382 mμ (ε 24500).

EXPERIMENTAL

2,6-Dimethyl-Δ^3-tetrahydrobenzaldehyde dimethyl acetal (IIa). a) To 15 g of 2,6-dimethyl-Δ^3-tetrahydrobenzaldehyde (I), 18.4 g of tetramethoxysilane and a solution of 1 ml of hydrochloric acid in 0.4 ml of anhydrous methyl alcohol were added. The mixture stood for 3 days at room temperature, and then was treated with 50 ml

of 30% sodium hydroxide solution; the oil which floated to the surface was separated and washed with water. The wash waters were extracted with ether. The ethereal extract was combined with the oil layer and dried with potash. On distillation 3.2 g (21.3%) of the original aldehyde, b.p. 60-63° (8 mm), n_D^{20} 1.4668 and 12 g (77%) of 2,6-dimethyl-Δ^3-tetrahydrobenzaldehyde dimethyl acetal were obtained.

B.p. 82–84°(8 mm), n_D^{20} 1.4609, d_{20}^{20} 0.949, MR 53.61; Calc. 53.37.

Found %: C 71.95, 71.86; H 10.80, 10.86. $C_{11}H_{20}O_2$. Calculated %: C 71.70; H 10.89.

Tarry residue 2.5 g.

b) A solution of 20 g of the aldehyde in 80 ml of anhydrous methyl alcohol and 0.75 ml of hydrochloric acid (d 1.18) stood for 3 days at room temperature and then was treated with 70 ml of saturated soda solution and extracted with ether. The ethereal extracts were dried with potash. On distillation 3 g (15%) of the original aldehyde, b.p. 52-60° (2.5 mm), n_D^{20} 1.4660 and 15.5 g (70%) of the dimethyl acetal, b.p. 74–76° (2.5 mm), n_D^{20} 1.4609 and 2 g of a tarry residue were obtained.

c) A mixture of 20 g of the aldehyde, 24.5 g of tetraethoxysilane, 4 ml of anhydrous methyl alcohol, and 0.3 ml of 85% phosphoric acid stood at room temperature for 3 days. The mixture, which had become quite dark, was treated with 30% alkali, and the separated oil, combined with ethereal extracts from the alkaline solution, was washed with water and dried with potash. After four distillations 3.5 g (13.4%) of the acetal, b.p. 76–77.5° (5 mm), n_D^{20} 1.4620.

2,6-Dimethyl-Δ^3-tetrahydrobenzaldehyde diethyl acetal (IIb) [3]. a) A solution of 53 g of 2,6-dimethyl-Δ^3-tetrahydrobenzaldehyde (I), 80 g of tetraethoxysilane, 1.5 ml of hydrochloric acid (d 1.18), and 56 ml of anhydrous alcohol stood for 3 days at room temperature. After the usual treatment there were obtained 14 g (26.7%) of the original aldehyde, b.p. 64-70° (8 mm), n_D^{20} 1.4660, 51 g (62%) of 2,6-dimethyl-Δ^3-tetrahydrobenzaldehyde diethyl acetal, b.p. 68-70° (1 mm), n_D^{20} 1.4532, and 2 g of a tarry residue.

b) A mixture of 15 g of the aldehyde, 25.2 g of tetraethoxysilane, 0.3 ml of 85% phosphoric acid, and 0.64 ml of anhydrous alcohol was kept for 3 days at room temperature. After the usual treatment there were obtained 5 g of the original aldehyde, b.p. 60–80° (8 mm), n_D^{20} 1.4630, 4 g (17.4%) of the diethylacetal, b.p. 99–100° (8 mm), n_D^{20} 1.4543 and 5 g of a tarry residue.

c) A mixture of 10 g of the aldehyde, 13 g of orthoformic ester, 50 ml of anhydrous alcohol, and 1 ml of p-toluenesulfonic acid stood for 24 hours at room temperature, after which it was diluted with 90 ml of ether, washed with 90 ml of saturated soda solution, and dried with potash. On distillation 12.5 g (90%) of the diethyl acetal, b.p. 70–71° (1 mm), n_D^{20} 1.4530.

The same result was obtained when boron trifluoride etherate was used as catalyst.

2,6-Dimethyl-Δ^3-tetrahydrobenzaldehyde dibutyl acetal (IIc). A mixture consisting of 39 g of 2,6-dimethyl-Δ^3-tetrahydrobenzaldehyde (I), 46 g of n-butyl alcohol, 45 ml of n-hexane, and 0.05 g of p-toluenesulfonic acid was heated for 10 hours in an apparatus provided with a distilling receiver. During this time 4 ml of water was collected. The reaction mass was treated with 30 ml of saturated soda solution, and the organic layer was separated, and dried with potash. On distillation there were obtained 6.3 g (16.2%) of the original aldehyde, b.p. 34–50° (2 mm), n_D^{20} 1.4670 and 50 g (81.5%) of 2,6-dimethyl-Δ^3-tetrahydrobenzaldehyde dibutyl acetal.

B.p. 109–112°(1 mm), n_D^{20} 1.4600, d_{20}^{20} 0.9038, MR 81.29; Calc. 81.12.

Found %: C 76.31, 76.38; H 11.80, 11.63. $C_{17}H_{32}O_2$. Calculated %: C 76.12; H 11.94.

Tarry residue 2 g.

2,6-Dimethylhexahydrobenzaldehyde dimethyl acetal (IIIa). A solution of 20 g of 2,6-dimethyl-Δ^3-tetrahydrobenzaldehyde dimethyl acetal (IIa) in 200 ml of anhydrous methyl alcohol was shaken in a current of hydrogen in the presence of 1 g of 6% $Pd/BaSO_4$. During 5 hours 2560 ml of hydrogen was absorbed, which corresponds to the calculated quantity. The catalyst was filtered out, the alcohol driven off, and the hydrogenation product distilled in vacuo. There was obtained 19.2 g (95%) of 2,6-dimethylhexahydrobenzaldehyde dimethyl acetal.

B.p. 73–75° (2.5 mm), n_D^{20} 1.4523, d_{20}^{20} 0.9301, MR 53.98; Calc. 54.08.

Found %: C 71.17, 71.23; H 11.70, 11.98. $C_{11}H_{22}O_2$. Calculated %: C 70.96; H 11.77.

2,6-Dimethylhexahydrobenzaldehyde diethyl acetal (IIIb) was similarly obtained, in 98% yield. B.p. 84–87° (2.6 mm), n_D^{20} 1.4451 [3].

2,6-Dimethylhexahydrobenzaldehyde dibutyl acetal (IIIc) was obtained in 97% yield.

B.p. 101–102° (2 mm), n_D^{20} 1.4528, d_{20}^{20} 0.8936, MR 81.61; Calc. 81.79.

Found %: C 75.57, 75.63; H 12.27, 12.33. $C_{17}H_{34}O_2$. Calculated %: C 75.55; H 12.59.

1-Bromo-2,6-dimethylhexahydrobenzaldehyde dimethyl acetal (IVa). To a solution of 24 g of 2,6-dimethylhexahydrobenzaldehyde dimethyl acetal (IIIa) in 120 ml of chloroform with vigorous stirring, cooling, and illumination with a 300 w lamp a solution of 20.6 g of bromine in 65 ml of chloroform was added dropwise. The reaction mass was kept at a temperature from -7 to -5°. When the bromine addition was finished, 60 ml of anhydrous methyl alcohol was added. The mixture was kept at room temperature for 5 hours and then treated with 200 ml of 2 N alkali solution, the mixture being cooled to 5°; then the chloroform layer was separated, and the water layer was extracted three times with chloroform. The chloroform extract was dried with potash. On distillation there was obtained 6.4 g (26.6%) of the original dimethyl acetal, b.p. 55–64° (0.5 mm) and 16.2 g (64.5%) of 1-bromo-2,6-dimethylhexahydrobenzaldehyde dimethyl acetal.

B.p. 68–70° (0.5 mm), n_D^{20} 1.4925, d_{20}^{20} 1.2380, MR 62.09; Calc. 61.85.

Found %: C 49.67, 49.75; H 7.81, 8.06. $C_{11}H_{21}O_2Br$. Calculated %: C 49.81; H 7.92.

1-Bromo-2,6-dimethylhexahydrobenzaldehyde diethyl acetal (IVb) was similarly obtained, in 69% yield.

B p. 83–85° (0.5 mm), n_D^{20} 1.4820, d_{20}^{20} 1.182, MR 70.67; Calc. 71.09.

Found %: C 53.00, 53.10; H 8.43, 8.21. $C_{13}H_{25}O_2Br$. Calculated %: C 53.24; H 8.53.

1-Bromo-2,6-dimethylhexahydrobenzaldehyde dibutyl acetal (IVc) was obtained in 61% yield.

B.p. 115–118° (0.2 mm), n_D^{20} 1.4822, d_{20}^{20} 1.113, MR 89.46; Calc. 89.55.

Found %: C 58.57, 58.66; H 9.18, 9.31. $C_{17}H_{33}O_2Br$. Calculated %: C 58.50; H 9.45.

2,6-Dimethyl-Δ^1-tetrahydrobenzaldehyde dimethyl acetal (Va). A mixture of 7.2 g of 1-bromo-2,6-dimethylhexahydrobenzaldehyde dimethyl acetal (IVa) and 15 g of powdered potassium hydroxide was vigorously stirred for 2 hours at 110°. Then 20 ml of water was added and the organic layer extracted with ether and dried with potash. After two distillations there was obtained 3.2 g (63%) of 2,6-dimethyl-Δ^1-tetrahydrobenzaldehyde dimethyl acetal.

B.p. 59–61° (1.5 mm), n_D^{20} 1.4641, d_{20}^{20} 0.9498, MR 53.46; Calc. 53.61.

Found %: C 71.98, 71.65; H 11.12, 11.06. $C_{11}H_{20}O_2$. Calculated %: C 71.73; H 10.87.

The 2,4-dinitrophenylhydrazone obtained was recrystallized twice from alcohol: it then melted at 162.5-163.5°, λ_{max} 382 mμ (ε 24500).

2,6-Dimethyl-Δ^1-tetrahydrobenzaldehyde diethyl acetal (Vb). A mixture of 10 g of 1-bromo-2,6-dimethylhexahydrobenzaldehyde diethyl acetal (IVb) and 19.2 g of powdered potassium hydroxide was stirred for 2.5 hours at 120-130° After the usual treatment there was obtained 4.1 g (56%) of 2,6-dimethyl-Δ^1-tetrahydrobenzaldehyde diethyl acetal.

B.p. 70–71° (1.5 mm), n_D^{20} 1.4580, d_{20}^{20} 0.9168, MR 62.97; Calc. 62.85.

Found %: C 74.25, 74.33; H 11.03, 11.20. $C_{13}H_{24}O_2$. Calculated %: C 74.10; H 11.14.

2,6-Dimethyl-Δ^1-tetrahydrobenzaldehyde dibutyl acetal (Va). A mixture of 13 g of 1-bromo-2,6-dimethylhexahydrobenzaldehyde dibutyl acetal and 20.5 g of powdered potassium hydroxide was vigorously stirred for 2.5 hours at 140-150°. After the usual treatment there was obtained 5.5 g (55%) of 2,6-dimethyl-Δ^1-tetrahydrobenzaldehyde dibutyl acetal.

B.p. 91–94° (1 mm), n_D^{20} 1.4597, d_{20}^{20} 0.9010, MR 81.41; Calc. 81.32.

Found %: C 76.33, 75.98; H 11.87, 11.64. $C_{17}H_{32}O_2$. Calculated %: C 76.12; H 11.93.

1-Methoxymethylene-2,6-dimethylcyclohexene-2 (VI). A mixture of 7 g of 1-bromo-2,6-dimethylhexahydrobenzaldehyde dimethyl acetal (IVa) and 12.2 g of diethylaniline was heated for 2 minutes at 220°. Then the reaction mass was quickly cooled, and the substance which crystallized was dissolved in 15 ml of water, the organic layer separated, and the water layer extracted three times with ether (60 ml). The ethereal extract, combined with the organic layer, was washed three times with 15 ml of 6% hydrochloric acid and then with saturated soda solution, and dried with potash. On distillation there was obtained 1.7 g of a substance with b.p. 52-54° (2 mm), n_D^{20} 1.5000, λ_{max} 247.5 mμ (ϵ 27500).

Found %: C 71.56, 71.62; H 9.68, 9.80. $C_{10}H_{16}O$. Calculated %: C 71.48; H 9.52.

The 2,4-dinitrophenylhydrazone obtained was bright-red; it melted at 162.5-163.5°.

SUMMARY

1. 2,6-Dimethyl-Δ^1-tetrahydrobenzaldehyde dimethyl, diethyl, and dibutyl acetals were prepared.

2. It was shown that dehydrobromination of 1-bromo-2,6-dimethylhexahydrobenzaldehyde acetals at temperatures above 200° leads to the formation of cyclic alkoxydienes.

3. 2,6-Dimethyl-Δ^1-tetrahydrobenzaldehyde acetals are obtained in good yields on dehydrobromination of the corresponding α-bromosubstituted acetals with powdered potassium hydroxide.

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*Original Russian pagination. See C. B. translation

SYNTHESIS OF ACYL-2-CHLOROCYCLOHEXENES-2 AND ETHYLENE KETALS OF 2-ACYLCYCLOHEXANONES

NEW SYNTHESIS OF PHENANTHRENES

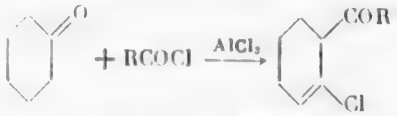
N. K. Kochetkov, É. E. Nifant'ev and V. N. Shibaev

Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2275-2282, July, 1960
Original article submitted July 6, 1959

β-Dicarbonyl compounds are key materials in organic synthesis, and hence the search for ways of preparing new members of this important class and their further use in synthetic chemistry is of substantial interest. In the present article we report the synthesis of previously unknown 2-acylcyclohexanone ethylene ketals, which are interesting starting materials and were used by us, in particular, for the development of a new, convenient method for the synthesis of phenanthrene derivatives.

The starting compounds for the preparation of 2-acylcyclohexanone ethylene ketals were acyl-2-chlorocyclohexenes-2, which were prepared through the condensation of cyclohexanone with acid chlorides in the presence of aluminum chloride. We studied this reaction in detail in the case of the interaction of cyclohexanone with acetyl chloride, and advanced a hypothesis on its mechanism [1]. Now we have extended the reaction to new objectives, and propose it as a general method of synthesizing acyl-2-chlorocyclohexenes-2.



R = CH_3, C_2H_5, iso-C_4H_9.

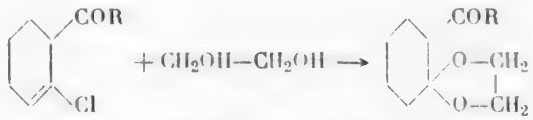
The reaction is most conveniently carried out in dichloroethane; carbon disulfide and carbon tetrachloride, as solvents, give poorer results. To obtain optimum yields, about 3 moles or at least 2 moles each of aluminum chloride and the acid chloride must be used per mole of ketone, for reasons inherent in the mechanism of this reaction. The reaction mixture is stirred for 20-30 hours at room temperature, it being necessary to increase the reaction time as the molecular weight of the acid chloride increases. Carrying out the reaction at a higher temperature or for a longer time markedly increases resinification.

The synthesized unsaturated chloroketones are oily substances, stable on keeping; contrary to the analogous compounds obtained in the cyclopentane series [1,2], whose double bond lies in the α, β-position, the described compounds have a double bond in the β,γ-position and are acyl-2-chlorocyclohexenes-2. This follows from the absence in them of exaltation of molar refraction, characteristic of both the corresponding cyclopentane derivatives [2] and aliphatic β-chlorovinyl ketones [3]. The absence of a conjugated system in the synthesized compounds is confirmed also by UV spectra obtained from their 2,4-dinitrophenylhydrazones, which have an absorption maximum characteristic of unconjugated ketones (344-345 mμ in isooctane, 362 mμ in alcohol). It is not impossible that a slight admixture of a conjugated ketone—an acyl-2-chlorocyclohexene-1 [cf. 1]—is formed in the interaction of cyclohexanone with acid chlorides, since the resulting preparations boil in a range of several degrees; however, as will be evident below, this does not in the least hinder their further synthetic use.

The interesting question as to why an unconjugated ketone is formed when cyclohexanone is used in the reaction being investigated, whereas a conjugated one is formed with cyclopentanone, is difficult to answer comprehensively at this time. It is known that the action of acids and especially bases leads to mutual transitions of α, β- and β, γ-unsaturated carbonyl compounds; this is the so-called "three-carbon tautomerism" [4,6]. In the case of cyclohexene compounds the three-carbon tautomeric equilibrium is usually shifted toward the formation of β, γ-unsaturated structures [cf. 7]. The formation of α, β-unsaturated isomers, on the contrary, is characteristic of cyclopentene compounds [8, 9]. Obviously this difference in the behavior of five-and six-membered rings is due to their difference in conformation. It may be thought that the decisive feature in the formation of the β, γ-isomer in the cyclohexene series is the difference due to relative energies in the stability of axial and equatorial substituents on the one hand and quasiequatorial and quasiaxial ones on the other in the cyclohexene compound formed on elimination of the elements of acetic acid from the intermediate reaction product. Owing to the lack of sufficient material on the conformation of the cyclohexene ring, however, this question cannot be analyzed in detail.

The halogen atom in the acyl-2-chlorocyclohexenes-2 obtained does not have the high mobility characteristic of this atom in β-chlorovinyl ketones [3]; this is evidently due not only to the absence of conjugation in the system, which would provide transmission of influence to the β-carbon atom to which the chlorine is attached, but also to the presence of a cyclic system which hinders halogen exchange; we have considered this in detail in the case of the corresponding cyclopentane derivatives [2]. Nevertheless, some halogen-exchange reactions can be carried out. Thus on interaction with alcoholic alkali or sodium phenoxide, the halogen atom is exchanged and β-phenoxy- or β-alkoxyvinyl ketones are formed. However, this reaction is not of preparative value, since it goes in several directions, being complicated by side-processes, as a result of which a mixture of substances is formed, which is difficult to resolve.

In the interaction of acyl-2-chlorocyclohexenes-2 with ethylene glycol, which we used earlier to prepare β-ketoaldehyde ethylene acetals from β-chlorovinyl ketones [2, 10, 11], 2-acylcyclohexanone ethylene ketals are formed.

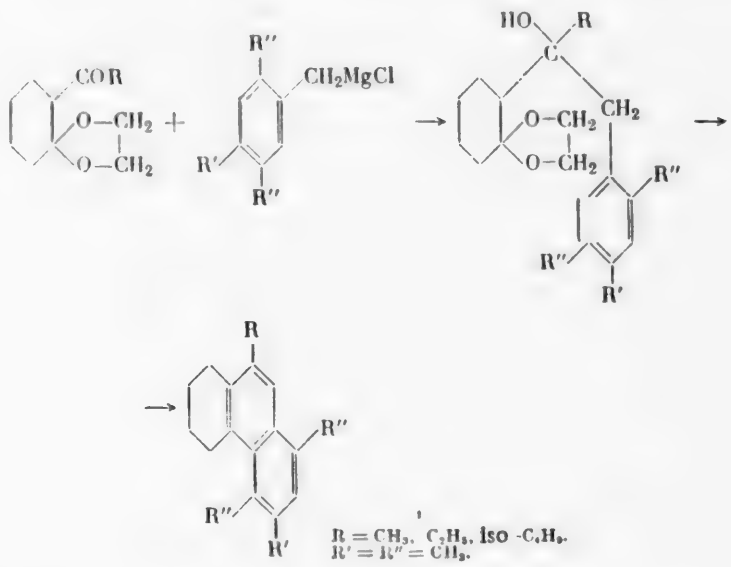


R = CH_3, C_2H_5, iso-C_4H_9.

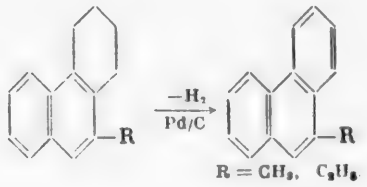
This reaction is most conveniently carried out with dioxane as solvent. Yields of 2-acylcyclohexanone ethylene ketals are 50-60%. Halogen exchange proceeds with more difficulty in this case in comparison either with β-chlorovinyl ketones or acyl-2-chlorocyclopentenes-1. On the basis of certain observations it may be assumed that in the course of the reaction the original chloride is first isomerized to a conjugated chloride—an acyl-2-chlorocyclohexene-1 which then reacts with ethylene glycol like other β-chlorovinyl ketones. Naturally, a slight admixture of the indicated conjugated chloride (see above) in the original chloride does not affect the result of the reaction. The ethylene ketals obtained are stable, colorless oils. Their structure was confirmed in the case of the simplest member—2-acetylcyclohexanone ethylene ketal—by a positive reaction for the acetyl group and by hydrolysis with dilute acid, leading to 2-acetylcyclohexanone, which was identified in the form of the copper salt. 2-Acylcyclohexanone ethylene ketals in which one of the carbonyl groups is protected are interesting starting materials for synthesis. We developed a new synthesis of the phenanthrene system, based on them. This synthesis is similar to that of the naphthalene nucleus, developed earlier in our laboratory [10, 12], and is carried out according to the scheme shown below.

The interaction of ethylene ketals with benzylmagnesium chloride gives the corresponding hydroxyketals, which can be isolated as individuals if necessary. The latter is unnecessary, however, and the hydroxyketals obtained may, without purification, be converted by aromatic cyclodehydration to 1,2,3,4-tetrahydrophenanthrenes. On investigating this step we tried various condensing agents. The best results are obtained with hydrogen bromide in acetic acid, or a mixture of concentrated sulfuric and phosphoric acids, the latter variant of the reaction being experimentally more convenient. Polyphosphoric acid gives lower yields. The tetrahydrophenanthrenes may be isolated by distillation. The reaction products are most conveniently purified through formation of the picrates with subsequent decomposition by passing solutions of the picrates through aluminum oxide. By this method we obtained several previously unknown 10-alkyl-1,2,3,4-tetrahydrophenanthrenes in 25-55% yields, reckoned on the original ethylene ketals (two steps). Subsequent experiments in this direction showed that the scope of the reac-

action may be extended. Thus we obtained 6,10-dimethyl-1,2,3,4-tetrahydrophenanthrene from 4-methylbenzylmagnesium chloride, and 5,8,10-trimethyl-1,2,3,4-tetrahydrophenanthrene from 2,5-dimethylbenzylmagnesium chloride. It should be noted that yields in the latter case are somewhat lower (14 and 17%), which is explained by the complexity of formation of organomagnesium compounds from substituted benzyl chlorides. However, data on a new method of preparing the corresponding organolithium compounds appeared recently in the literature [13], so that it may be hoped that various polysubstituted phenanthrenes can be prepared conveniently and in high yields on the basis thereof.



The structures of the compounds obtained were confirmed by their UV spectra, which had absorption bands in the 230-320 mμ region, characteristic of the tetrahydrophenanthrene nucleus. The tetrahydrophenanthrenes obtained are quantitatively dehydrogenated to the corresponding 9-alkylphenanthrenes on heating with palladium on charcoal.



This conversion conclusively proves the structure of the tetrahydrophenanthrenes obtained. Moreover, the described conversion may be recommended as a convenient synthesis of 9-alkylphenanthrenes.

In conclusion it should be noted that the proposed new method of synthesizing derivatives of phenanthrenes differs favorably from existing multistep syntheses both in its simplicity and in the availability of the starting materials.

EXPERIMENTAL

Acetyl-2-chlorocyclohexene-2. Into a three-neck flask provided with a stirrer, a reflux condenser protected from atmospheric moisture, and a dropping funnel, 11 g of aluminum chloride and 150 ml of dry dichloroethane were put. A mixture of 36.5 g of cyclohexanone and 86 g of acetyl chloride was added with vigorous stirring and cooling by water at room temperature; the mixture was stirred for 18 hours and then decomposed with ice to which 15 ml of concentrated hydrochloric acid had been added. The organic layer was separated, and the water layer was extracted three times with dichloroethane. The combined extracts were washed with water and dried over calcium chloride. The solvent was driven off in a slight vacuum and the residue distilled, the fraction with b.p. 105-120° (20 mm) being collected. After redistillation there was obtained 49.5 g (82%) of a substance with b.p. 124-129° (30 mm). After a third distillation the substance had the following constants:

B.p. 108–109° (15 mm), n_D^{20} 1.4985, d_4^{20} 1.1332, MR_D 41.38. $C_9H_{13}OClF$. Calculated 41.35.

Found %: C 60.33; 60.33; H 7.09, 7.11; Cl 22.29, 22.46. $C_8H_{11}OCl$. Calculated %: C 60.56; H 7.00; Cl 22.35.

Literature data for the reaction product of cyclohexanone and acetyl chloride [14]: b.p. 93-98° (9 mm), n_D^{20} 1.4952, d_4^{20} 1.1187.

The 2,4-dinitrophenylhydrazone consisted of yellow crystals with m.p. 128-129° (from alcohol), λ_{max} 344 mμ (isooctane); 365 mμ (alcohol).

Literature data for acetyl-2-chlorocyclohexene-2 2,4-dinitrophenylhydrazone [15]: m.p. 128-129° (from alcohol), λ_{max} 362 mμ (alcohol).

Propionyl-2-chlorocyclohexene-2. This was prepared as in the preceding experiment from 77.5 g of cyclohexanone, 144 g of propionyl chloride, and 211 g of aluminum chloride in 200 ml of dichloroethane, the reaction time being 24 hours; 80 g (59%) of the substance, b.p. 99-108° (8 mm), was obtained. After repeated distillation the substance had the constants:

B.p. 102–103° (9 mm), n_D^{20} 1.4932, d_4^{20} 1.0903, MR_D 46.05. $C_9H_{13}OClF$. Calculated 45.97.

Found %: Cl 20.42, 20.30. $C_9H_{13}OCl$. Calculated %: Cl 20.53.

Literature data for the reaction product of cyclohexane and propionyl chloride [14]: b.p. 113-116° (12 mm), n_D^{20} 1.4901, d_4^{20} 1.0931.

The 2,4-dinitrophenylhydrazone consisted of yellow needles with m.p. 109–110° (from alcohol), λ_{max} 345 mμ (isooctane).

Found %: N 15.29, 15.50. $C_{15}H_{17}O_4N_4Cl$. Calculated %: N 15.78.

Isovaleryl-2-chlorocyclohexene-2. This was prepared as in the preceding from 49 g of cyclohexanone, 120 g of isovaleryl chloride, and 134 g of aluminum chloride in 200 ml of dichloroethane, the reaction time being 41 hours; there was obtained 46.5 g (45%) of isovaleryl-2-chlorocyclohexene-2, b.p. 115-120° (8 mm), n_D^{20} 1.4842. After redistillation the substance had the constants:

B.p. 70–71° (0.5 mm), n_D^{20} 1.4859, d_4^{20} 1.0420, MR_D 55.30. $C_{11}H_{17}OClF$. Calculated 55.21.

Found %: C 66.02, 65.83; H 8.62, 8.59. $C_{11}H_{17}OCl$. Calculated %: C 65.83; H 8.53.

2-Acetylcyclohexanone ethylene ketal. Into a three-neck flask provided with a stirrer, a dropping funnel, and a reflux condenser with a tube containing soda-lime, a solution of 7.2 g of potassium hydroxide in 50 ml of glycol was put. Sixty ml of dioxane was added and the mixture heated to boiling. Then 19.7 g of acetyl-2-chlorocyclohexene-2 was added dropwise with vigorous stirring, and the mixture was boiled and stirred for 5 hours.* The cooled reaction mixture was poured into water and extracted four times with ether, the extracts dried with magnesium sulfate, and the solvent distilled off. On fractionation of the residue in vacuo there was obtained 13.9 g (61%) of acetylcyclohexanone ethylene ketal. After redistillation the substance had the constants:

B.p. 121–122° (10 mm), n_D^{20} 1.4781, d_4^{20} 1.1197, MR_D 46.91; Calc. 47.28.

Found %: C 66.01, 65.22; H 8.69, 8.76. $C_{10}H_{16}O_3$. Calculated %: C 65.21; H 8.74.

The product was a colorless oil, soluble in common organic solvents. It was stable on keeping. On shaking with ferric chloride solution it gradually gave a violet color. It gave a reaction for the acetyl group with o-nitrobenzaldehyde [16].

2-Propionylcyclohexanone ethylene ketal. This was prepared similarly from 19 g of propionyl-2-chlorocyclohexene-2, 6.4 g of potassium hydroxide in 60 ml of glycol, and 60 ml of dioxane; after boiling for 7 hours there was obtained 10.8 (50%) of 2-propionylcyclohexanone ethylene ketal.

B.p. 123–124° (8 mm), n_D^{20} 1.4745, d_4^{20} 1.0808, MR_D 51.59; Calc. 51.90.

Found %: C 66.58, 66.41; H 9.27, 9.17. $C_{11}H_{18}O_3$. Calculated %: C 66.64; H 9.08.

* When the quantities of starting materials were increased, the reaction time had to be greatly increased.

The product was a colorless oil, soluble in common organic solvents and stable on keeping.

2-Isovalerylcyclohexanone ethylene ketal. This was prepared similarly from 12 g of isovaleryl-2-chlorocyclohexene-2, 3.45 g of potassium hydroxide, 25 ml of glycol, and 30 ml of dioxane, the reaction time being 7 hours; there was obtained 8.7 g (64%) of 2-isovalerylcyclohexanone ethylene ketal.

B.p. 96–97° (0.5 mm), n_D^{20} 1.4727, d_4^{20} 1.0413, MR_D 60.94; Calc. 61.14.

Found %: C 68.83, 68.82; H 9.83, 9.92. $C_{13}H_{22}O_3$. Calculated %: C 69.09; H 9.80.

The product was a colorless oil, soluble in common organic solvents. It was stable on keeping.

Hydrolysis of 2-acetylcyclohexanone ethylene ketal. A 2.5 g quantity of 2-acetylcyclohexanone ethylene ketal was dissolved in 15 ml of alcohol, mixed with a solution of 0.2 ml of concentrated hydrochloric acid in 25 ml of water, and refluxed for 5 minutes. The mixture was poured into an equal volume of water and extracted with ether, the extracts dried with magnesium sulfate, the ether distilled off, and the residue diluted with an equal volume of methanol and treated with hot, saturated aqueous copper acetate solution. After cooling, the gray-green β-diketone copper salt separated; it was filtered out, washed with petroleum ether, and dried. It had m.p. 157–158° and gave no depression with a known sample of the copper salt of 2-acetylcyclohexanone [17].

2-(2'-Methyl-2'-hydroxyphenethyl) cyclohexanone ethylene ketal. To the benzylmagnesium chloride solution prepared in the usual manner from 4.8 g of magnesium and 27.7 g of benzyl chloride in 70 ml of absolute ether, 33.7 g of 2-acetylcyclohexanone ethylene ketal in 40 ml of absolute ether was added with vigorous stirring, the flask being cooled in a freezing mixture. The reaction mixture was stirred and boiled for 2 hours and then decomposed with ammonium chloride solution. The reaction product was extracted with ether and the extracts dried over magnesium sulfate. After distilling off the solvent there was obtained 34 g (70.5%) of colorless needles with m.p. 67–68° (from aqueous methanol).

Found %: C 73.12, 73.19; H 9.11, 9.05. $C_{16}H_{24}O_3$. Calculated %: C 72.71; H 9.15.

1,2,3,4-Tetrahydro-10-methylphenanthrene. a) Cyclization by a mixture of hydrobromic and acetic acids. A solution of 8.9 g of 2-(2'-methyl-2'-hydroxyphenethyl)cyclohexanone ethylene ketal in 180 ml of glacial acetic acid was heated to boiling, 25 ml of 42% hydrobromic acid was added all at once, and the mixture was boiled for 7.5 hours; on cooling, it was poured into water and the hydrocarbon extracted with benzene. The extracts were washed with water until all traces of acid were removed, dried over calcium chloride, and the benzene driven off in a slight vacuum. The residual oil was distilled in vacuo, the 117–120° (0.8 mm) fraction being collected; the latter soon crystallized completely. Yield of 1,2,3,4-tetrahydro-10-methylphenanthrene, 2.15 g (31.5%), m.p. 42.5–43° (from petroleum ether cooled by a dry ice-acetone mixture).

Found %: C 91.66, 91.42; H 8.35, 8.61. $C_{15}H_{16}$. Calculated %: C 91.77, H 8.20.

The product consisted of colorless crystals, readily soluble in ether, benzene, and other solvents and less soluble in alcohol.

The UV spectrum (in methanol) had the characteristic maxima:: λ_{max} 233, 275, 285, 318; lg ε 4.98, 3.69, 3.73, 2.51.

The picrate was obtained in alcohol, and consisted of orange needles with m.p. 137–137.5° (from alcohol).

Found %: N 9.72, 9.73. $C_{21}H_{19}O_7N_3$. Calculated %: N 9.88.

b) Cyclization by a mixture of sulfuric and phosphoric acids. To a cold mixture of 10 g of concentrated sulfuric acid and 6.2 g of 80% phosphoric acid, cooled with a snow-salt mixture, 5.2 g of 2-(2'-methyl-2'-hydroxyphenethyl)cyclohexanone ethylene ketal was added in small portions, with stirring. The reaction mixture was heated for 2 hours in a boiling water bath and then poured into ice and treated as in the preceding experiment. The benzene was distilled off and the substance converted to the picrate. There was obtained 2.13 g of 1,2,3,4-tetrahydro-10-methylphenanthrene picrate, which corresponds to a 26% yield of the hydrocarbon.

c) Cyclization by polyphosphoric acid. A mixture of 5.2 g of the original ethylene ketal and 52 g of polyphosphoric acid was heated at 80–85° for 4 hours. The reaction mixture was decomposed by stirring with water, and treated as in the preceding experiment. There was obtained 1.4 g (16%) of 1,2,3,4-tetrahydro-10-methylphenanthrene picrate.

9-Methylphenanthrene. A 0.2 g quantity of 1,2,3,4-tetrahydro-10-methylphenanthrene was heated with 0.1 g of palladium catalyst on charcoal (10% palladium) for 3 hours at 294-298°. The resulting white crystals, which sublimed on the walls of the flask, had m.p. 87.5–88°. They gave a picrate consisting of yellow needles with m.p. 148–149° (from alcohol).

Literature data for 9-methylphenanthrene: m.p. 90–91°, picrate m.p. 151–153° [18] and m.p. 88–89°, picrate m.p. 151-153° [19].

1,2,3,4-Tetrahydro-10-ethylphenanthrene. To a solution of benzylmagnsium chloride (from 7.55 g of benzyl chloride and 1.46 g of magnesium in 50 ml of absolute ether), 6.9 g of 2-propionylcyclohexanone ethylene ketal in 30 ml of absolute ether was added with stirring and cooling; the mixture was boiled for 2 hours, decomposed with chloride solution, extracted with ether, the extracts dried over magnesium sulfate, and the ether distilled off. There was obtained 13.85 g of an oil, which on cooling was mixed with a cold mixture of 26.2 g of concentrated sulfuric acid and 17 g of 80% phosphoric acid. The mixture was heated for 15 minutes at 65-70°, cooled, and poured into ice. The hydrocarbon was extracted with benzene and the latter distilled off in a slight vacuum. The residue was treated with an equal weight of picric acid, dissolved in hot alcohol. There was obtained 6.3 g (41% reckoned on the ethylene ketal) of 1,2,3,4-tetrahydro-10-ethylphenanthrene picrate. After recrystallization from alcohol the picrate had m.p. 151-152°. It consisted of orange needles, readily soluble in ether and benzene.

Found %: N 9.62, 9.45. $C_{22}H_{21}O_7N_3$. Calculated %: N 9.56.

1,2,3,4-Tetrahydro-10-ethylphenanthrene was liberated from the picrate by passing a benzene solution of the latter through a column containing aluminum oxide, followed by elution with benzene in the form of a yellowish, viscous oil with n_D^{20} 1.6166.

Found %: C 91.26, 91.09; H 9.05, 9.05. $C_{16}H_{18}$. Calculated %: C 91.37; H 8.63.

Characteristic maxima in the UV absorption spectrum: λ_{max} 232, 275, 385, 317 mμ; lg ε 4.58, 3.80, 3.81, 2.69.

9-Ethylphenanthrene. A 113 mg quantity of 1,2,3,4-tetrahydro-10-ethylphenanthrene was heated with 0.2 g of 10% palladium on charcoal at 260-270° for 3.5 hours. The contents of the flask were treated with ether, the solution filtered, the ether distilled off, and alcoholic picric acid solution added to the residue. 9-Ethylphenanthrene picrate, m.p. 120-121° (from alcohol) [18], was obtained.

1,2,3,4-Tetrahydro-10-isobutylphenanthrene. This was prepared similarly from 0.85 g of benzyl chloride and 5.5 g of 2-isobutylcyclohexanone ethylene ketal in 50 ml of absolute ether. The ether was distilled off, and the residue was treated for 15 minutes at 65-70° with a mixture of 15 ml of sulfuric acid and 10 ml of 80% phosphoric acid. 1,2,3,4-Tetrahydro-10-isobutylphenanthrene was isolated by distillation, the fraction with b.p. 110-130° (0.5 mm) being collected; the latter crystallized on standing, forming colorless crystals with m.p. 73-75° (from methanol). Yield 2.6 g (53%, reckoned on the original ethylene ketal).

The UV spectrum of the hydrocarbon was similar to those of other homologs: λ_{max} 233, 285, 315 mμ (inflection) (in methanol); lg ε 4.98, 3.78, 2.17.

The trinitrobenzene complex consisted of yellow needles with m.p. 106–107° (from alcohol).

Found %: N 8.89, 8.96. $C_{24}H_{25}O_6N_3$. Calculated %: N 9.31.

1,2,3,4-Tetrahydro-6,10-dimethylphenanthrene. This was prepared as described above from 2.45 g of ω-chloro-p-xylene, 0.4 g of magnesium, and 2.6 g of 2-acetylcyclohexanone ethylene ketal through cyclization by a mixture of 10.4 g of sulfuric acid and 6.8 g of phosphoric acid; there was obtained 0.8 g (14%, reckoned on the original ethylene ketal) of 1,2,3,4-tetrahydro-6,10-dimethylphenanthrene picrate, m.p. 139–140° (from alcohol).

Found %: N 9.72, 9.67. $C_{22}H_{21}O_7N_3$. Calculated %: N 9.56.

1,2,3,4-Tetrahydro-5,8,10-trimethylphenanthrene. To 4.45 g of magnesium powder and 2.85 g of magnesium turnings activated by heating with iodine, in 100 ml of absolute ether in a nitrogen atmosphere, 11.6 g of chloromethyl-p-xylene in 100 ml of absolute ether was added during 1.5 hours. The resulting solution of the organomagnesium compound was cooled with ice, and a solution of 5.9 g of 2-acetylcyclohexanone ethylene ketal in an equal volume of ether was added. The reaction mixture was left overnight and then decomposed with ammon-

ium chloride solution. It was extracted with ether, the extracts dried with magnesium sulfate, the ether distilled off, and the residue cyclized by a mixture of 22 g of concentrated sulfuric acid and 14.6 g of phosphoric acid for 15 minutes at 65–70°. After the usual treatment there was obtained 4.9 g of a viscous, brown mass. Four g of the reaction product, treated in the usual manner, gave 1.97 g of the picrate, dark-red crystals, m.p. 109–110° (from alcohol).

Found %: N 9.01, 8.84. $C_{23}H_{23}O_7N_3$. Calculated %: N 9.27.

SUMMARY

1. A method was developed for synthesizing acyl-2-chlorocyclohexenes-2 through the condensation of cyclohexanone with acid chlorides in the presence of aluminum chloride (yields 45-80%).

2. A method was developed for synthesizing 2-acylcyclohexanone ethylene ketals through the interaction of acyl-2-chlorocyclohexenes-2 with ethylene glycol in the presence of alkali (yields 50-65%).

3. A new method is proposed for synthesizing phenanthrene derivatives through the condensation of 2-acylcyclohexanone ethylene ketals with compounds of the benzylmagnesium chloride type, with subsequent aromatic cyclodehydration of the hydroxyketals formed.

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CONDENSATION OF ALDEHYDES AND KETONES

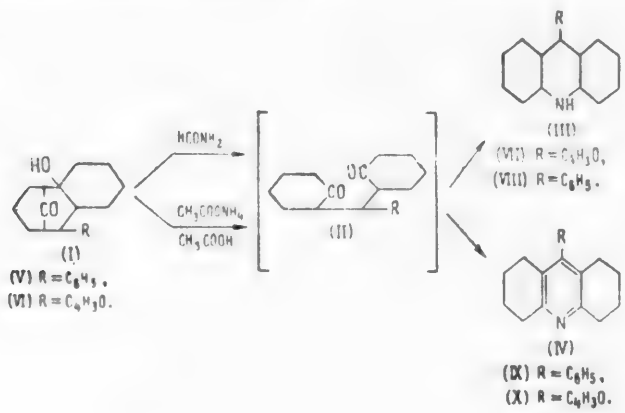
VI. CONVERSION FROM PHENYL- AND FURYLTRICYCLOHEXANOLONES TO 9-PHENYL- AND FURYLHYDROACRIDINES

M. N. Tilichenko and V G. Kharchenko

Saratov State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2283-2285, July, 1960
Original article submitted July 8, 1959

In our laboratory to achieve conversion from the cycloketol form (I) to the 9-R-perhydroacridine (III), the Leichardt reaction (heating with formamide) has been used successfully [1-3]. The reaction takes place very smoothly and with almost quantitative yield of bases (III); only in the case of tricyclohexanolone (I, R=H), besides perhydroacridine, a rather large quantity (about 33%) of symm -octahydroacridine is formed as well [1].



In the present communication we describe the extension of this reaction to furyltricyclohexanolone [2-furyl-3, 4-tetramethylene-bicyclo (3,3,1)-nonanone-9-ol-4] (VI), synthesized by us earlier [4] by the method of diketone condensation of cyclohexanone with furfurol.

The reaction here proceeds easily—markedly more easily than with the phenylketol (V) (see [3]). It is probable that this is connected with the more difficult solubility of the latter in formamide. However, with regard to yield of bases there is no difference between furyl- and phenylketols: both ketols are almost identically quantitatively converted into the corresponding bases (VII)and (VIII), which are obtained as N-formyl derivatives, easily hydrolyzed by alkalies.

To achieve conversion of phenyl-(V) and furyl (VI)-tricyclohexanolones into the corresponding octahydroacridines (IX and X) we used "the improved pyridine synthesis of Chichibabin" [5]. This reaction was applied to alicyclic ketones by Colonge and co-workers [6] and in the case of bicyclohexanones they obtained the corresponding symm -octahydroacridines. Our ketols, in the reactions represented in the scheme, are doubtless first of all isomerized into 1,5-bicyclohexanones (II), from which the corresponding hydroacridine compounds are then

formed. This supposition was confirmed experimentally by one of us in conjunction with Vysotskii [1] and Abramova [2]; it was shown that 1,5-diketones and cycloketols, isomeric to those of form (I), give one and the same result, with identical yields of hydroacridine. Thus, it was expected that ketols (V) and (VI) in the reaction of Chichibabin mentioned above would give bases (IX) and (X). Reactions of the compounds obtained confirmed fully these expectations, and the structure of the base obtained (IX) was proven by its catalytic dehydrogenation into 9-phenylacridine.

EXPERIMENTAL*

1. N-Formyl-9-furylperhydroacridine.

15.5 g of furylketol with m.p. 185-186°C [4] and 20 g of formamide [7] were heated as described earlier [3]. At 110° (in other cases at 97°C**), evolution of carbon dioxide bubbles began. At 120-130° evolution of gas proceeded more vigorously and continued for about 30 minutes. Heating was then discontinued, and the homogeneous mixture crystallized on cooling. The crystals were washed on a filter with water and dried on an earthenware dish. Yield 9 g, m.p. 208-209° (from dioxane); white prismatic small stick-like crystals. The substance was soluble in alcohol, benzene, and dioxane, insoluble in water.

Found %: HCO 9.81. $C_{18}H_{25}O_2N$. Calculated %: HCO 10.10.

From the filtrate and water washings, after they had been made alkaline with caustic soda, 7 g of 9-furylperhydroacridine was isolated, following purification by two distillations in vacuo.

9-Furylperhydroacridine (VII). N-Formyl-9-furylperhydroacridine was easily hydrolyzed by brief heating with 0.3-0.5 N alcoholic caustic soda solution; on dilution with water the free base settled out. From 9 g of formyl derivative 7.2 g of base was obtained. Total yield was 14.2 g (97%); white prismatic small stick-like crystals readily soluble in the usual organic solvents: m.p. 76-77° (from ether); b.p. 158-160° (2 mm).

Found %: C 78.50, 78.66; H 9.42, 9.76; N 5.81, 5.66. M 263, 259. $C_{17}H_{25}ON$. Calculated %: C 78.76; H 9.65; N 5.41. M 259.

A picrate was formed on mixing hot alcoholic solutions of the base and picric acid. Yellow elongated hexagons, m.p. 218-220 (from alcohol).

Found %: N 11.81, 11.97. $C_{23}H_{28}O_8N_4$. Calculated %: N 11.48.

The hydrochloride was formed as colorless small thin stick-like crystals, tapered at both ends, by passing dry hydrogen chloride into a benzene solution of the base. At 245-250° the crystals charred without melting; readily soluble in water.

Found %: Cl 11.55, 11.75. $C_{17}H_{26}ONCl$. Calculated %: Cl 12.01.

2. Synthesis of symm-octahydroacridines. Method. Phenyl-(V) or furyl-(VI)-ketol (1 part by weight), ammonium acetate (3-4 parts by weight), and acetic acid (3.5-6 parts by weight) were heated for 2 hours at 133-137°. The cooled mixture was saturated with concentrated soda solution until an alkaline reaction was obtained. The solid precipitate was isolated, washed with water, and crystallized from acetone.

9-Furyl-symm-octahydroacridine (X). Yield of the double-crystallized base was 74%. White prismatic small stick-like crystals soluble in ether, benzene, and, with greater difficulty, in alcohol, dioxane, and acetone; insoluble in water. M.p. 121-122° (from acetone).

Found %: C 80.61, 81.12; H 7.64, 7.82; N 5.45, 5.56. M 243, 246. $C_{17}H_{19}ON$. Calculated %: C 80.63; H 7.51; N 5.53. M 253.

The picrate (as described above) took the form of greenish-yellow prismatic small stick-like crystals, obliquely tapered at the ends, with m.p. 184-185° (from alcohol).

Found %: N 11.44, 11.64. $C_{23}H_{22}O_8N_4$. Calculated %: N 11.62.

The hydrochloride was obtained by passing dry hydrogen chloride into an ethereal solution of the base. The colorless small stick-like crystals were dissolved in water, recrystallized from alcohol, and charred at 210° without melting.

* With the assistance of students V. N. Dyukareva and N. A. Pelageicheva.

** Possibly owing to the nonstandard strength of the formamide prepared, due to the presence of $HCOONH_4$ and HCOOH as impurities.

Found %: Cl 11.76, 11.93. $C_{17}H_{20}ONCl$. Calculated %: Cl 12.22.

9-Phenyl-symm -octahydroacridine (IX). White prismatic small stick-like crystals, with m.p. 177-178° (from an acetone-alcohol mixture—7:1); solubility as for (X).

Found %: C 87.07, 86.88, H 8.38, 8.09; N 5.72, 5.32. M 265, 260. $C_{19}H_{21}N$. Calculated %: C 86.69; H 8.00; N 5.32. M 263.

The picrate (as described above) took the form of greenish-yellow prismatic small stick-like crystals tapering at the ends, with m.p. 175-175.5° (from alcohol).

Found %: N 11.57, 11.44. $C_{25}H_{24}O_7N_4$. Calculated %: N 11.38.

The hydrochloride was obtained by passing dry hydrogen chloride into a benzene solution of IX. White prismatic small stick-like crystals; readily soluble in water and alcohol. M.p. 243-245° (decomposing) (from an acetone-alcohol mixture, 20:1).

Found %: Cl 11.75. $C_{19}H_{21}N \cdot HCl$. Calculated %: Cl 11.85.

Dehydrogenation. 1 g of base (IX) and 0.21 g of Pt/C [8] were heated in a flask; hydrogen evolution began at 240° and ceased at 313°. 290 ml (0°, 760 mm) of a gas was collected, which corresponded to 0.013 mole of H_2 (calculated, 0.015 mole). The reaction product was extracted with ether; m.p. 180-181° (from benzene). A sample mixed with authentic 9-phenylacridine (m.p. 180-181.5°) melted without depression of melting point; greenish-yellow crystals.

SUMMARY

1. On being reacted with formamide, furyltricyclohexanolone is converted almost quantitatively into 9-furylperhydroacridine.

2. On being reacted with ammonium acetate in acetic acid, furyl-and phenyltricyclohexanolones are converted quite smoothly into symmetric 9-furyl-and 9-phenyloctahydroacridines.

3. 9-Phenyl-symm -octahydroacridine is dehydrogenated in the presence of Pt/C into 9-phenylacridine.

The hydroacridines listed have not been described in the literature.

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REACTIONS OF HYDRAZINE DERIVATIVES

XXIX. CYANOETHYLATION OF PYRAZOLONES

A. N. Kost, S. I. Suminov, R. S. Sagitullin, and V. V. Ershov

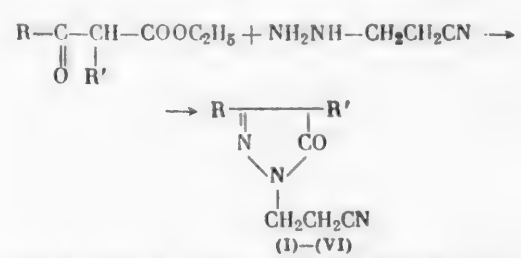
Moscow State University

Translated from Zhurnal Obshchei Khimii Vol. 30, No. 7, pp. 2286-2291,
July, 1960
Original article submitted July 15, 1959

Cyanoethylation of pyrazolones has not been described in the literature; moreover, there are indications [1] that 1-phenyl-3-methylpyrazolone does not react with acrylonitrile. However, our experiments showed that in the presence of alkali pyrazolones readily combine with acrylonitrile. In this case it could be expected that combinations with acrylonitrile would take place at the hydroxyl group of the tautomeric form of pyrazolone (hydroxypyrazole), at the amide nitrogen, or at the methylene bond (in the 4-position). To establish the structure of the product, we synthesized pyrazolones with the β-cyanoethyl group in a known position, i.e., in positions 1 and 4.

In the synthesis of 1-(β-cyanoethyl)-pyrazolones-5 we made use of the reaction of β-hydrazinopropionitrile with esters of β-keto-acids. In the patent literature [2,3] the possibility is shown of obtaining 3-methyl-1-(β-cyanoethyl)-pyrazolone-5 and 3-phenyl-1-(β-cyanoethyl)-pyrazolone-5 by this method, but the products were not defined by their constants, nor by analyses.

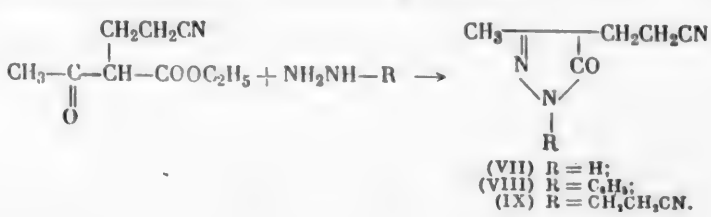
According to our data, the reaction of β-hydrazinopropionitrile with esters of various β-keto-acids in an alcoholic medium takes place on gentle heating and after a short period of boiling; the corresponding 1-(β-cyanoethyl)-3,4-dialkylpyrazolones-5 are formed in good yields (65-95%).



(I)–(VI)

(I) R = CH_3, R′ = H; (IV) R = C_6H_5, R′ = H;
(II) R = iso-C_3H_7, R′ = H; (V) R = R′ = CH_3;
(III) R = iso-C_4H_9, R′ = H; (VI) R = CH_3, R′ = C_4H_9.

We carried out synthesis of pyrazolones with a β-cyanoethyl group in the 4-position, starting from the monocyanoethylated acetoacetic ester and the corresponding hydrazines.



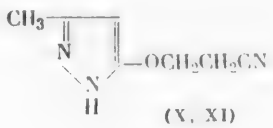
(VII) R = H;
(VIII) R = C_6H_5;
(IX) R = CH_2CH_2CN.

In the literature there are indications [4] that in the pyrazolone series the reaction of alkyl halides with sodium derivatives of pyrazolones can proceed predominantly through the oxygen atom. We therefore attempted the preparation also of the third possible product of cyanoethylation, namely, the β-cyanoethyl ester of 3-methyl-5-hydroxypyrazole. To this end, the cyanoethylation of 3-methylpyrazolone-5 was carried out by the action of β-chloropropionitrile in an alkaline medium under conditions permitting complete enolization of pyrazolone (the equivalent quantity of sodium in tert-butyl alcohol), whereupon a mixture was obtained of two substances which were separated by fractional crystallization. These substances (X and XI) had an identical elemental constitution, corresponding to a product of monocyanoethylation, did not give the violet coloration with ferric chloride solution characteristic of enols, and did not differ in melting point or degree of solubility in water. A melting point test on a mixture of both substances, nevertheless, did not give a melting point depression and had the same melting point as the low-melting form.

In their constants and properties both these substances differed markedly from the pyrazolones obtained earlier with the cyanoethyl group in the 1- and 4-positions (I and VII). A good yield of a mixture of these same substances is also formed on heating 3-methylpyrazolone-5 with acrylonitrile in an alkaline medium (a catalytic quantity of tert-sodium butylate).

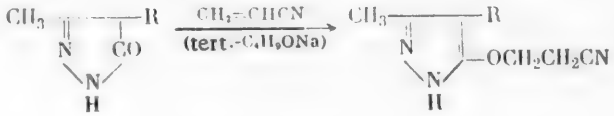
Similar results were obtained by carrying out cyanoethylation with an equivalent quantity of sodium or by using absolute tert-butyl alcohol as the solvent.

Compounds (X) and (XI) have identical infrared spectra, different both from the spectra of the initial 3-methylpyrazolone and the spectra of other β-cyanoethylpyrazolones. In them are clearly evident lines characteristic of C≡N and C=N (in a ring), lines of the carbonyl group being absent. The absorption spectra in the ultraviolet region (photographed by B. V. Lokshin) for all the pyrazolones investigated by us do not have characteristic extremes (maximum absorption occurs in the region where $\lambda < 200$ mμ), but the form of the curve for compounds (X) and (XI) is identical and also differs somewhat from other pyrazolones in showing a crest. All this permits the acceptance for compounds (X-XI) of the structure of β-cyanoethyl esters of 3-methyl-5-hydroxypyrazole, and the explanation of their difference by the presence of crystal modifications.



(X, XI)

Cyanoethylation of 4-(β-cyanoethyl)-3-methylpyrazolones-5 also takes place at the hydroxy-group, giving the corresponding β-cyanoethyl ester.



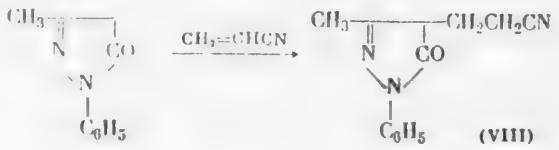
An attempt to introduce a cyanoethyl group at the nitrogen of 3-methylpyrazolone by transcyanoethylation (heating mixtures of equivalent quantities of dimethylaminopropionitrile hydrochloride and 3-methylpyrazolone-5 in dimethylaminopropionitrile for 2 hours at 160-170°C) was unsuccessful.

Cyanoethylation of 3-methylpyrazolone-5 in the 4-position by heating in a sealed ampoule in an acetic acid medium with catalytic additions of cuprous chloride also failed. In both cases pronounced resinification of the reaction mixture was observed.

Interesting results were obtained by the action of acrylonitrile on 3-methyl-1-phenylpyrazolone-5 in a strongly alkaline medium (excess tert-sodium butylate.).

Bruson [1] considered that cyanoethylation of 3-methyl-1-phenylpyrazolone-5 does not proceed because of the increased acidity of this compound, existing predominantly in the enol form. According to our observations, 3-methyl-1-phenylpyrazolone-5 is easily cyanoethylated in the presence of alkaline agents; moreover, the β-cyanoethyl group enters at the 4-position, giving an 85% yield of 4-(β-cyanoethyl)-3-methyl-1-phenylpyrazolone,

which proves to be identical with the pyrazolone (VIII), obtained by the reaction of the β-cyanoethylacetoacetic ester with phenylhydrazine in an acetic acid medium.



(VIII)

In this manner, on cyanoethylation of pyrazolones, formation of β-cyanoethyl esters of hydroxypyrazoles (O-cyanoethylation, in the enol form) occurs. In the presence of a phenyl group in the 1-position, transfer of the center of reaction and C-cyanoethylation (in the 4-position) occurs under the action of alkali.

EXPERIMENTAL

1-(β-Cyanoethyl)-3-methylpyrazolone-5 (I). To 8.5 g of β-hydrazinopropionitrile [5] in 15 ml of alcohol with cooling and stirring 13 g of freshly distilled acetoacetic ester was added, the mixture heated on a water bath for 15 minutes, alcohol and water distilled off in vacuo (20-30 mm), and the residue recrystallized from benzene. Yield 13.5 g (90%)). 1-(β-Cyanoethyl)-3-methylpyrazolone-5 readily dissolved in almost all polar solvents. M.p. 111-111.5° [2].

Found %: C 55.79, 55.70; H 6.16, 6.08. $C_7H_9ON_3$. Calculated %: C 55.61; H 6.00.

IR-spectrum of 3-methylpyrazolone (cm^{-1}): 736–744 (s), 818, 974 (s), 1001 (s), 1196, 1260, 1466 (s), 1512–1532, 1630 (s).

IR-spectrum of 1-(β-cyanoethyl)-3-methylpyrazolone-5 (cm^{-1}): 747 (s), 804, 830, 925, 966, 1040 (s), 1140, 1207, 1240, 1284, 1390, 1462, 1554, 2210 (med).

1-(β-Cyanoethyl)-3-isopropylpyrazolone-5 (II). Obtained similarly to the above from 1.82 g of β-hydrazinopropionitrile and 3.2 g of isobutyrylacetic ester in 2 ml of alcohol. Yield 2.5 g (66%), m.p. 121.5° (from benzene).

Found %: C 60.60, 60.62.* $C_9H_{13}ON_3$. Calculated %: C 60.31.

1-(β-Cyanoethyl)-3-isobutylpyrazolone-5 (III). Obtained from 1.7 g of isovalerylacetic ester and 0.85 g of β-hydrazinopropionitrile. Yield 1.5 g (78%), m.p. 92.5-93.5° (from benzene).

Found %: C 62.46, 62.10; N (nitrile) 7.17, 7.36. $C_{10}H_{15}ON_3$. Calculated %: C 62.15; N (nitrile) 7.25.

1-(β-Cyanoethyl)-3-phenylpyrazolone-5 (IV). Obtained from 3.9 g of benzoylacetic ester and 1.7 g of β-hydrazinopropionitrile in 15 ml of alcohol. The crystals settling out after cooling were filtered off, and washed with cold alcohol. Yield 4.0 g (94%), m.p. 184° (from alcohol).

Found %: N 19.54, 19.63. $C_{12}H_{11}ON_3$. Calculated %: N 19.71.

1-(β-Cyanoethyl)-3,4-diamethylpyrazolone-5 (V). Obtained from 2.9 g of α-methylacetoacetic ester in 3 ml of alcohol and 1.7 g of β-hydrazinopropionitrile. After cooling, the solution was diluted with ether and the crystals separating out gradually filtered off. Yield 2.2 g (67%), m.p. 132° (from a mixture of benzene and alcohol).

Found %: N 25.61, 25.69. $C_8H_{11}ON_3$. Calculated %: N 25.44.

1-(β-Cyanoethyl)-3-methyl-4-butylpyrazolone-5 (VI). Obtained similarly to the above from 1.7 g of α-butylacetoacetic ester in 3 ml of alcohol and 0.9 g of β-hydrazinopropionitrile. Yield 1.5 g (72%), m.p. 109-110° (from a large quantity of petroleum ether).

Found %: N 20.14, 20.21. $C_{11}H_{17}ON_3$. Calculated %: N 20.27.

4-(β-Cyanoethyl)-3-methylpyrazolone-5 (VII). To an emulsion of 13 g of α-(β-cyanoethyl)-acetoacetic ester [7] in 40 ml of water, 4 g of hydrazine hydrate in 15 ml of water was gradually added, and the mixture heated on a water bath for 0.5 hour. After cooling, the pyrazolone separated out in almost quantitive yield, m.p. 218°. After recrystallization from water m.p. increased to 219.5°.

* Part of the analysis was done by the wet combustion method, in which hydrogen determination is impossible.

Found %: C 55.54, 55.34; H 5.90, 6.00; N (nitrile) 9.41, 9.43. $C_7H_9ON_3$. Calculated %: C 55.61; H 6.00; N (nitrile) 9.26.

IR-spectrum (cm^{-1}): 724, 776 (s), 840, 862, 950 (s), 994, 1046, 1088, 1168, 1196, 1213 (s), 1426, 1458-1462, 1538, 2210 (med).

If 3.4 g of α-(β-cyanoethyl)-acetoacetic ester and 1.2 g of hydrazine hydrate in 2 ml of glacial acetic acid are used in the reaction, and the mixture heated on a water bath for 1 hour, yield of pyrazolone amounts to 2.3 g (75%).

4-(β-Cyanoethyl)-3-methyl-1-phenylpyrazolone-5 (VIII). To 3.65 g of monocyanoethylated acetoacetic ester in 3 ml of glacial acetic acid 2.2 g of phenylhydrazine was added dropwise, and the mixture heated on a water bath for 1 hour. The completely solidified mass was recrystallized from a large quantity of dilute methyl alcohol.

Yield 4.2 g (98%), m.p. (after several recrystallizations from water) 160-160.5°.

Found %: C 68.92, 69.04; N (nitrile) 6.53, 6.61. $C_{13}H_{13}ON_3$. Calculated %: C 68.70; N (nitrile) 6.16.

1,4-Di-(β-cyanoethyl)-3-methylpyrazolone-5 (IX). To 17.5 g of α-(β-cyanoethyl)-acetoacetic ester 8.2 g of β-hydrazinopropionitrile was added dropwise, and the mixture heated on a water bath for 45 minutes. The product that gradually crystallized out was carefully ground with small portions of ether, and filtered off. Yield 14.3 g (74%), m.p. 128.5-129.5° (from a large quantity of a benzene-acetone mixture).

Found %: C 58.94, 58.92; H 5.91; 6.08. $C_{10}H_{12}ON_4$. Calculated %: C 58.81; H 5.92.

The Reaction of 3-Methylpyrazolone-5 with β-Chloropropionitrile. To a solution of tert-sodium butylate (2 g of metallic sodium in 75 ml of tert-butyl alcohol) 8.7 g of 3-methylpyrazolone-5 was added. The mixture was heated with stirring until completely homogeneous, and 8 g of β-chloropropionitrile was added over a period of 0.5 hours. The reaction mixture was then heated on a water bath for 30 minutes, cooled, the solvent distilled off in vacuo, and the residue recrystallized from a minimum quantity of water. 9.3 g (69.7%) of a substance was obtained with m.p. 162-163°, on fractional crystallization of which two forms of the β-cyanoethyl ester of 3-methyl-5-hydroxypyrazole separated out. Neither compound gave a coloration with ferric chloride solution.

The first form (X) with m.p. 175° was obtained on fractional crystallization from water.

Found %: C 56.08, 55.96; H 6.09, 6.08; N 28.22, 27.71. $C_7H_9ON_3$. Calculated %: C 55.62; H 6.00; N 27.80.

The second, with m.p. 191-191.5°, was obtained in only a very small yield—on evaporating the filtrates and recrystallizing the residue from alcohol.

Found %: C 55.82, 55.74; H 6.08, 6.06. $C_7H_9ON_3$. Calculated %: C 55.61; H 6.00.

The melting point of the mixture of products corresponded to the low-melting form (175°).

IR-spectra (cm^{-1}): first modification (X)—748 (s), 794, 821, 825, 926, 987 (s), 1028, 1050, 1128, 1160, 1208-1234 (s), 1320, 1380 (med), 1460 (med), 1510-1550 (s), 2210 (s). Second modification (XI) – 746 (s), 774, 822, 844 (s), 923, 991, 1018, 1050, 1112, 1166, 1212-1240, 1319 (med), 1388 (med), 1466 (s), 1510-1550 (s), 2210 (s).

The Reaction of 3-Methylpyrazolone-5 with Acrylonitrile. To a solution of tert-sodium butylate (1.5 g of sodium in 125 ml of tert-butyl alcohol) 20 g of 3-methylpyrazolone-5 was added, the mixture heated with stirring until the pyrazolone was completely dissolved, then 13.5 g of acrylonitrile was added dropwise. The reaction mixture was boiled on a water bath for 1 hour, cooled, neutralized with concentrated hydrochloric acid, and transferred to a Claisen flask, from which the solvent was distilled off in vacuo; in this case, no tert-butoxypropionitrile was observed. The residue in the flask was recrystallized from a minimum quantity of water, the filtrate evaporated, and again recrystallized. Total yield of the β-cyanoethyl ester of 3-methyl-5-hydroxypyrazole was 23.6 g (76.5%), m.p. 163-163.5°. No melting point depression with the substance obtained in the preceding experiment was observed.

Found %: N 27.90, 27.79. $C_7H_9ON_3$. Calculated %: N 27.80.

The Reaction of 3-Methyl-4-(β-cyanoethyl)-pyrazolone-5 with Acrylonitrile. To a solution of tert-sodium butylate (0.69 g of metallic sodium in 40 ml of tert-butyl alcohol) 4.5 g of 3-methyl-4-(β-cyanoethyl)-pyrazolone-5 was added, the mixture heated with stirring for 0.5 hour, then, after cooling, 1.9 g of acrylonitrile was

added gradually and boiled for an additional 2 hours. The cold reaction mixture was neutralized with Congo diluted (1:4) with hydrochloric acid, and the crystals separating out were filtered off. 3.7 g (61%) of the β-cyanoethyl ester of 3-methyl-4-(β-cyanoethyl)-5-hydroxypyrazole was obtained, m.p. 194-195° (after recrystallization from water). The compound gave no coloration with ferric chloride solution. The melting point of a mixture of the initial 3-methyl-4-(β-cyanoethyl)-pyrazolone-5 was 183°.

Found %: N 27.60, 27.20. $C_{10}H_{12}ON_4$ Calculated %: N 27.44.

The Reaction of 1-Phenyl-3-methylpyrazolone-5 with Acrylonitrile. To a solution of tert-sodium butylate (1.0 g of sodium in 30 ml of tert-butyl alcohol) 5.2 g of 1-phenyl-3-methylpyrazolone-5 was added, the mixture heated for 1 hour, 1.9 g of acrylonitrile added, and boiling continued for a further 2 hours. The cooled reaction mixture was neutralized with Congo diluted (1:4) with hydrochloric acid, and the crystals separating out filtered off. Yield of 3-methyl-1-phenyl-4-(β-cyanoethyl)-pyrazolone-5 was 5.2 g (85%), m.p. 159-160° (after two recrystallizations from water).

Found %: C 69.08, 69.12; H 5.88, 5.78. $C_{13}H_{13}ON_3$ Calculated %: C 68.70; H 5.76.

The melting point of a mixture with initial 3-methyl-1-phenylpyrazolone-5 gave a depression (m.p. 97-98°), and on melting this mixture with authentic 3-methyl-1-phenyl-4-(β-cyanoethyl)-pyrazolone-5 (VIII) no melting point depression was observed.

SUMMARY

1. It was found that pyrazolones can be cyanoethylated in an alkaline medium. 3-Methylpyrazolone-5- is cyanoethylated in the enol form, giving an ester of 5-hydroxypyrazole; but in the presence of a phenyl group bonded to the nitrogen atom, the reaction proceeds with transfer of the reaction center to the 4-position.

2. The synthesis of a series of 1-(β-cyanoethyl)-pyrazolones-5 by reacting β-hydrazinopropionitrile with esters of β-keto acids is described.

3. To synthesize C-cyancethylated pyrazolones, the monocyanoethylated acetcacetic ester was reacted with several hydrazines.

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THE REACTIONS OF DITERTIARY BUTYL PEROXIDES WITH MERCUROUS AND MERCURIC ACETATES, WITH BENZOATES OF MERCURIC OXIDE, AND WITH METALLIC MERCURY

Yu. A. Ol'dekop and M. M. Azanovskaya

Institute of Physicoorganic Chemistry, Academy of Sciences, BSSR
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2291-2294, July, 1960
Original article submitted July 10, 1959

Ditertiary butyl peroxide is widely used in industry as a polymerization initiator and as an initiator of other industrially important chemical processes. A considerable number of investigations have been carried out regarding its thermal decomposition in gaseous and liquid phases [1-3]; however, reactions of ditertiary butyl peroxide with mercury salts have received little study.

In an earlier published work [4] it was shown by one of us and T. V. Vasilevskaya that the methyl radical formed on decomposition of ditertiary butyl peroxide disrupts the Hg–O bond in mercuric pivalate (mercuric trimethylacetate) and gives a methyl mercuric compound.

In the present work we investigated the reactions of ditertiary butyl peroxide with mercurous and mercuric acetates, and with mercuric benzoate, as well as the possibility of bonding a methyl radical to metallic mercury.

During the reaction of the peroxide with mercurous acetate in acetic acid at 118°C, formation of methylmercury compounds (36%), of metallic mercury (64%), and of acetone took place. The gas consisted of CO_2, methane, ethane, and CO. Substitution of acetic acid by chlorobenzene led to a lower yield of methylmercury compounds (18%) and a higher yield of metallic mercury (75%). In the reaction products, acetic acid (50%) acetone, and unreacted mercurous acetate (6.7%) were observed. The gas consisted of CO_2, methane, and CO.

On substitution of mercurous acetate by mercuric acetate, yield of methylmercury compounds increased to 50%, and yield of metallic mercury decreased to 25%. Mercurous acetate and unreacted mercuric acetate were observed in the reaction products. CO_2 and methane were found in the gases.

Formation of a methylmercuric salt on reacting ditertiary butyl peroxide with mercuric benzoate proved the peroxide origin of the methyl radical in this salt.

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \quad (1)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + CH_3COCH_3 \quad (2)$$

$$(C_6H_5CO_2)_2Hg + CH_3\cdot \longrightarrow CH_3HgOCOC_6H_5 + C_6H_5CO_2\cdot \quad (3)$$

Yield of methylmercuric compounds amounted to 20%. Among the reaction products were found metallic mercury and benzoic acid. Phenylmercuric compounds were not observed. Methane and CO_2 were found in the gases.

The high yield of metallic mercury should be noted in the reaction of the peroxide with mercury salts, a particularly high yield of it being observed in the reaction with mercurous acetate. In a specially conducted experiment, on heating the reactants in the absence of ditertiary butyl peroxide, reduction of the mercurous salt to mercury was not observed.

We also investigated the decomposition of ditertiary butyl peroxide in acetic acid in the presence of some metallic mercury. We succeeded in fixing a methyl radical directly on to mercury, as was proved by the formation of methylmercury compounds.

Methyl mercury compounds were identified in all experiments in a similar manner to that described previously [5].

EXPERIMENTAL

Experiments were carried out in an apparatus consisting of a three-necked flask, fitted with a mechanical stirrer and reflux condenser to which was attached a gas burette. Heating continued intermittently for 6-8 hours. The course of the reaction was controlled according to the evolution of gaseous products. In all experiments, gas formation ceased after 19-22 hours. (In the final experiment no gas was collected.) Gases were analyzed in a VTI-2 apparatus.

The Reaction of Ditertiary Butyl Peroxide with Mercurous Acetate in Acetic Acid. 10.4 g of mercurous acetate, 2.92 g of ditertiary butyl peroxide, and 70 g of glacial acetic acid were heated with stirring at the boiling point of acetic acid. As heating proceeded the mercury salt dissolved, and formation of metallic mercury took place. After 22 hours, evolution of gas ceased, and heating was discontinued. 46 ml of a gas was collected which consisted of carbon dioxide, carbon monoxide, methane, and ethane.

The acetic acid solution was combined with the metallic mercury. 5.1 g, or 64%, of mercury was collected, calculated on the salt used in the reaction. The solution was distilled in vacuo at low pressure. 65.8 g of liquid was collected. In it was found acetone, identified by means of its 2,4-dinitrophenylhydrazone. 2,4-Dinitrophenylhydrazone has a m.p. of 126°; a sample mixed with the authentic 2,4-dinitrophenylhydrazone of acetone melted at the same temperature. The residue from the vacuum distillation crystallized on cooling to room temperature. Weight of residue 6.8 g. The residue was extracted with boiling water and then treated with concentrated potassium iodide solution. A precipitate of methylmercury iodide then separated out, its weight amounting to 4.9 g (36%), m.p. 142-143°; a sample mixed with authentic methylmercury iodide melted at 142°.

The Reaction of Ditertiary Butyl Peroxide with Mercurous Acetate in Chlorobenzene. 10.4 g of mercurous acetate, 2.92 g of ditertiary butyl peroxide, and 50 g of chlorobenzene were heated at 120°. After several hours, formation of metallic mercury was observed on the bottom and walls of the flask. After 19 hours evolution of gases ceased. 55 ml of gas was collected, consisting of carbon dioxide, carbon monoxide, and methane.

A dark-colored liquid separated from the residue. From the residue 6.1 g (75%) of mercury was collected. In addition, 0.7 g (6.7%) of unreacted initial salt was obtained.

Found %: Hg 77.4. $C_4H_6O_4Hg_2$. Calculated %: Hg 77.3.

The solvent was distilled from the filtrate in vacuo. In an aqueous extract of the solvent were observed acetone (the 2,4-dinitrophenylhydrazone melted at 126°) and acetic acid amounting to 1.21 g (50%). The residue obtained after solvent distillation was extracted with boiling water. 2.45 g (18%) of methylmercury iodide, m.p. 142-143°, was precipitated from the aqueous solution by potassium iodide. A sample mixed with authentic methylmercury iodide did not give a melting point depression.

The Reaction of Ditertiary Butyl Peroxide with Mercuric Acetate in Acetic Acid. 6.36 g of mercuric acetate, 2.92 g of ditertiary butyl peroxide, and 70 g of glacial acetic acid were heated at the boiling point of acetic acid for 19 hours. At this point evolution of gases ceased. The gas consisted of carbon dioxide and methane. A yellow-brown solution separated from the metallic mercury. Weight of the latter amounted to 1 g (25%). The solution was distilled in vacuo, 66.6 g of distillate being collected. A brown-colored liquid remained in the flask, from which liquid, on treatment with boiling water, a precipitate separated out, amounting to 1.3 g (25%), this proving to be a mixture of mercurous (0.7 g) and mercuric (0.6 g) salts. After separation of the precipitate, the filtrate was treated with potassium iodide; 3.4 g (49.8%) of methylmercury iodide separated out, m.p. 142°. A sample of a mixture of this and authentic methylmercury iodide melted at 142-143°.

The Reaction of Ditertiary Butyl Peroxide with Mercuric Benzoate in Chlorobenzene. 8.87 g of mercuric benzoate (obtained from sodium benzoate and mercuric acetate; found %: Hg 45.21. $C_{14}H_{10}O_4Hg$. Calculated %: Hg 45.37). 2.92 g of ditertiary butyl peroxide, and 75 ml of chlorobenzene were heated with stirring at the

boiling point of the solvent for 20 hours. 34 ml of gas was collected, consisting of methane and carbon dioxide. On completion of the reaction the precipitate was filtered off. 0.88 g (22%) of mercury was obtained. The residue remaining after separation of mercury weighed 1.21 g (12%) and contained 40.2% mercury (by microanalysis). The residue was not examined more closely. The filtrate underwent distillation of chlorobenzene in vacuo at 50 mm. After chlorobenzene distillation, in the residue was an oily product from which benzoic acid was extracted with aqueous methanol. Its weight amounted to 1.1 g, m.p. 121°; melting point depression was not observed with an authentic specimen of benzoic acid. 1.4 g (20%) of methylmercury iodide, m.p. 142°, was obtained from the aqueous methanol extract after addition of potassium iodide; a sample mixed with pure methylmercury iodide also melted at 142°.

In the residue was 3 g of a viscous, oily product, not investigated more closely.

The Reaction of Ditertiary Butyl Peroxide with Mercury in Acetic Acid.* 2.0 g of ditertiary butyl peroxide, 40 g of mercury, and 100 ml of acetic acid were heated with stirring at the boiling point of acetic acid for 20 hours. On cooling, mercury separated from the solution. The solution underwent vacuum distillation. 10% KI was added to the residue. 0.28 g of methylmercury iodide, m.p. 143°, was collected. Mercurous and mercuric acetates were not found.

SUMMARY

1. On reacting ditertiary butyl peroxide with mercurous acetate in boiling acetic acid, formation of methylmercury salts, metallic mercury, and acetone took place. In the gases evolved CO_2, methane, ethane, and CO were found.

In a chlorobenzene medium at 120°, methylmercury salts, mercury, acetic acid, acetone, CO_2, methane, and CO were found. In the reaction products, unreacted initial salt was observed.

2. On reacting ditertiary butyl peroxide with mercuric acetate in boiling acetic acid, methylmercury salts, metallic mercury, mercurous acetate, carbon dioxide, and methane were obtained. In the reaction products, unreacted initial salt was found.

3. On reacting ditertiary butyl peroxide with mercuric benzoate in boiling chlorobenzene, formation of methylmercury salts, mercury, and benzoic acid took place. The gas consisted of methane and CO_2.

4. For the first time in decomposition of ditertiary butyl peroxide a methyl radical was bonded to metallic mercury.

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* L. Sushchinskaya took part in this experiment.

** Original Russian pagination. See C. B. translation.

SUBSTITUTED PYRIDINES. 2,5-DIMETHYL-4-[p(o)-TOLYL]-PYRIDINES AND THEIR CONVERSIONS

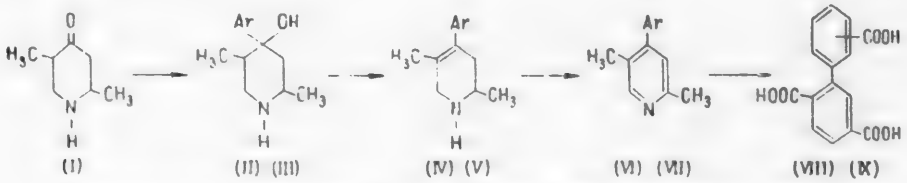
N. S. Prostakov, N. N. Mikheeva, A. V. Igumnova, and G. I. Zimina

Moscow Institute of Fine Chemical Technology

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2294-2297, July, 1960
Original article submitted July 13, 1959

Continuing our studies on the synthesis of substituted pyridines, which are of interest for obtaining physiologically active substances and also as the initial products in the synthesis of new condensation resins and polymeric materials containing the pyridine ring, we turned to the preparation of γ-substituted pyridines. These were synthesized by a method we had developed previously for the preparation of 2,5-dimethyl-4-phenylpyridine. The latter compound had been obtained in satisfactory yield by the dehydration of 2,5-dimethyl-4-phenyl-4-piperidol [1] with subsequent dehydrogenation of the 2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (on K-12 brand industrial catalyst) to 2,5-dimethyl-4-phenylpyridine [2].

The newly synthesized starting compounds 2,5-dimethyl-4-(p-tolyl)-4-piperidol (II) and 2,5-dimethyl-4-(o-tolyl)-4-piperidol (III) were obtained by the interaction of 2,5-dimethyl-4-piperidone (I) with p- and o-tolyllithium respectively, and also with p-tolyl magnesium bromide. These alcohols upon dehydration gave respectively 2,5-dimethyl-4-(p-tolyl)-1,2,3,6-tetrahydropyridine (IV) and 2,5-dimethyl-4-(o-tolyl)-1,2,3,6-tetrahydropyridine (V), which were dehydrogenated on K-12 brand catalyst to respectively 2,5-dimethyl-4-(p-tolyl)-pyridine (VI) and 2,5-dimethyl-4-(o-tolyl)-pyridine (VII).



(I) (II) (III) (IV) (V) (VI) (VII) (VIII) (IX)

for (II), (IV), (VI), (VIII) Ar = $C_6H_4CH_3$-p for (III), (V), (VII), (IX) Ar = $C_6H_4CH_3$-o

Oxidation of the indicated γ-aryl-substituted pyridines gave 4-(p-carboxyphenyl)-pyridine-2,5,-dicarboxylic acid (VIII) and 4-(o-carboxyphenyl)-pyridine-2,5-dicarboxylic acid (IX). Upon bromination of the substituted pyridine (VI), 2,5-dimethyl-4-(p-bromomethylphenyl)-pyridine was formed.

EXPERIMENTAL

2,5-Dimethyl-4-(p-tolyl)-4-piperidol (II), 2,5-Dimethyl-4-(p-tolyl)-1,2,3,6-tetrahydropyridine (IV), and 2,5-Dimethyl-4-(p-tolyl)-pyridine (VI).

a) To p-tolyl magnesium bromide (obtained from 53.9 g p-bromotoluene and 7.7 g magnesium in 600 ml absolute ether) 20 g 2,5-dimethyl-4-piperidone was added over two hours with ice-water cooling and with stirring. The mixture was heated for 2.5 hours (refluxing the ether). The reaction mixture after cooling was treated successively with 50 ml water, 50 ml 15% HCl, and 25 ml concentrated HCl. The water layer was saturated with potassium hydroxide. The organic bases were extracted with five 100 ml portions of ether. Vacuum distillation of the reaction products gave the following fractions: first, 56° (2.5 mm), 9.3 g (initial piperidone); second, 56-156° (2.5 mm),

1.8 g; third, 156-170° (2.5 mm), 5.8 g. Residue 1.5 g. The third fraction was crystallized from benzine. There was obtained 3.7 g of a mixture of stereoisomeric 2,5-dimethyl-4-(p-tolyl)-4-piperidols (II), from which one of the stereoisomeric piperidols (II) was isolated with m.p. 118-119° (from benzine).

Found %: N 6.78, 6.40. $C_{14}H_{21}ON$. Calculated %: N 6.39.

b) p-Tolyllithium was obtained from 16 g lithium and 200 g p-bromotoluene in 1000 ml absolute ether. With ice-water cooling and with stirring, 56 g 2,5-dimethyl-4-piperidone was added over one hour. The following day the reaction mixture was treated with 200 ml water, 200 ml 15% HCl, and then with 100 ml concentrated HCl. The aqueous layer of salts of the organic bases was separated, treated with sodium hydroxide, and then with ether. Distillation of the reaction products gave the following fractions: first, 65-104° (2.5 mm), 5 g, n_D^{17} 1.5162; second, 104-130° (2.5 mm), 16.9 g, n_D^{17} 1.5311; third, 130-180° (2.5 mm), 40.5 g (viscous barely pourable liquid). The third fraction was crystallized from benzine. There was obtained 16.4 g of a mixture of stereoisomeric 2,5-dimethyl-4-(p-tolyl)-4-piperidols (II) (m.p. 108-113°), from which there was separated by recrystallization from benzine the above-described form of the piperidol (II) with m.p. 118-119°.

A mixture of 16 g 2,5-dimethyl-4-(p-tolyl)-4-piperidol, 23 g 70% sulfuric acid, and 3.5 g calcined copper sulfate was heated four hours on a steam bath. Then the mixture was treated with sodium carbonate. The organic bases were extracted with ether and after drying were distilled. There was obtained 12.9 g 2,5-dimethyl-4-(p-tolyl)-1,2,3,6-tetrahydropyridine (IV) with b.p. 117-120° (2.5 mm), n_D^{18} 1.5559. An additional quantity of (IV) was recovered by the following means: From the mother liquor remaining after separation of the crystalline piperidol (II) (16.4 g) the benzine was distilled off. The residue, 30.8 g, was heated 2.5 hours on a steam bath with 44.3 g 70% sulfuric acid and 6.5 g copper sulfate. Further treatment was carried out as usual for the separation of the organic bases, which upon distillation gave the following fractions: first, 88-134° (5 mm), 2.9 g, n_D^{19} 1.5273; second 144-150° (5 mm), 9.9 g, n_D^{19} 1.5540 [2,5-dimethyl-4-(p-tolyl)-1,2,3,6-tetrahydropyridine]. The first fraction showed relatively rapid crystallization. From this fraction there were isolated crystals of a substance whose structure has not yet been determined, with m.p. 96-98° (from benzine).

2,5-Dimethyl-4-(p-tolyl)-pyridine was obtained from both samples of (IV). Dehydrogenation was carried out in a flow system on industrial catalyst (K-12 brand) by a method described in one of the preceding communications [2]. The volume of catalyst was 150 ml and the temperature in the catalyst zone was 395-400°. In 80 minutes 12 g of 2,5-dimethyl-4-(p-tolyl)-1,2,3,6-tetrahydropyridine was passed through the catalyst. There was collected 8.1 g of condensate, vacuum distillation of which gave 7.5 g of 2,5-dimethyl-4-(p-tolyl)-pyridine (VI).

B.p. 132° (3 mm), n_D^{20} 1.5811, d_{20}^{20} 1.0274, MR_D 63.91. $C_{14}H_{15}N_{F3}$. Calculated 63.59.

Gas collection was 2.4 liters (750 mm, 20°; CO_2 0.7%, H_2 99.3%).

2,5-Dimethyl-4-(o-tolyl)-4-piperidol (III), 2,5-Dimethyl-4-(o-tolyl)-1,2,3,6-tetrahydropyridine (V), and 2,5-Dimethyl-4-(o-tolyl)-pyridine (VII).

o-Tolyllithium was obtained from 186 g o-bromotoluene and 15.2 g lithium in 1000 ml absolute ether. Then 53.2 g 2,5-dimethyl-4-piperidone was added over one hour with vigorous stirring of the reaction mixture and ice-water cooling. The usual treatment was then carried out for separation of the organic bases from the reaction mixture; distillation of the bases gave the following fractions: first, 52-113° (2.5 mm), 9.3 g, n_D^{21} 1.5100; second, 113-137° (2.5 mm), 10.8 g, n_D^{21} 1.5265; third, 137-141° (2.5 mm), 17.41 g, n_D^{21} 1.5335; fourth, 141-160° (2.5 mm), 25.8 g. Residue after distillation, 7.5 g.

The fourth fraction was crystallized from benzine. 2,5-Dimethyl-4-(o-tolyl)-4-piperidol (III) was obtained with m.p. 78-79° (from benzine).

Found %: N 6.60, 6.20. $C_{14}H_{21}ON$. Calculated %: N 6.39.

22.3 g of the piperidol (III), 36 g 70% sulfuric acid, and 4.7 g calcined copper sulfate were heated on a steam bath for four hours. The mixture was treated with sodium carbonate. The organic bases were extracted with ether, then vacuum distilled. There was obtained 12 g 2,5-dimethyl-4-(o-tolyl)-1,2,3,6-tetrahydropyridine (V).

B.p. 125–127° (2.5 mm), n_D^{20} 1.5371, d_{21}^{21} 0.9695, MR_D 64.76 $C_{14}H_{19}N$. Calculated 64.19.

Methiodide - m.p. 230-232° (from alcohol).

Found %: N 4.40, 4.37. $C_{15}H_{22}NI$. Calculated %: N 4.09.

The dehydrogenation of the 2,5-dimethyl-4-(o-tolyl)-1,2,3,6-tetrahydropyridine was carried out as described above for the p-tolyl isomer (IV). The 2,5-dimethyl-4-(o-tolyl)-1,2,3,6-tetrahydropyridine (9.7 g dissolved in 10 ml benzene) was passed through the contacting tube (150 ml of K-12 brand catalyst) at constant rate for two hours. The catalyst zone temperature was 395-400°. Distillation of the catalyzate gave 5.2 g 2,5-dimethyl-4-(o-tolyl)-pyridine (VII).

B.p. 104-106° (1.5 mm), n_D^{21} 1.5686.

Found %: N 7.18, 7.53. $C_{14}H_{15}N$. Calculated %: N 7.11.

Picrate—m.p. 158-160° (from alcohol).

Found %: N 13.35, 13.53. $C_{20}H_{18}O_7N_4$. Calculated %: N 13.14.

During the dehydrogenation 2.2 liters of gas was collected (749 mm, 21°; C_nH_{2n} 1%, H_2 99%.

4-(p-Carboxyphenyl)-pyridine-2,5-dicarboxylic Acid (VIII). To a mixture of 5.9 g 2,5-dimethyl-4-(p-tolyl)-pyridine and 750 ml water (stirred vigorously at 100°) 28.4 g potassium permanganate was added in small portions over 3.5 hours. The manganese dioxide was filtered off and washed three times with hot water. The aqueous solution was evaporated under vacuum to 150 ml and then treated with dilute sulfuric acid up to acidic reaction with Congo red. The precipitated material was filtered off, washed with water, and recrystallized from aqueous alcohol. There was obtained 2.6 g of 4-(p-carboxyphenyl)-pyridine-2,5-dicarboxylic acid (VIII) with m.p. 244-245° (sealed capillary, decomp.).

Found %: N 4.86, 4.58. $C_{14}H_9O_6N$. Calculated %: N 4.88.

Trimethyl ester of 4-(p-carboxyphenyl)-pyridine-2,5-dicarboxylic acid—m.p. 130-132° (from benzine).

4-(o-Carboxyphenyl)-pyridine-2,5-dicarboxylic Acid (IX). To a mixture of 3.9 g 2,5-dimethyl-4-(o-tolyl)-pyridine and 500 ml water, at 100°, 19 g potassium permanganate was added in small portions over five hours. After separation of the manganese dioxide the aqueous solution was evaporated to 150 ml and treated with dilute sulfuric acid up to acidic reaction with Congo red. The precipitated material was separated and recrystallized from aqueous alcohol, giving 2.7 g 4-(o-carboxyphenyl)-pyridine-2,5-dicarboxylic acid (IX) with m.p. 221-223°.

Found %: N 5.17, 5.16. $C_{14}H_9O_6N$. Calculated %: N 4.88.

2,5-Dimethyl-4-(p-bromomethylphenyl)-pyridine. To a solution of 7 g 2,5-dimethyl-4-(p-tolyl)-pyridine in 50 ml glacial acetic acid, with vigorous stirring and strong illumination, a solution of 5.7 g bromine in 10 ml glacial acetic acid was added dropwise. The acid was removed by vacuum distillation. To the residue there was added 10 ml water and then sodium carbonate solution. The liberated oil was extracted with ether. After drying with sodium sulfate and distilling off the ether, there was obtained 6.7 g of crystals of 2,5-dimethyl-4-(p-bromomethylphenyl)-pyridine with m.p. 234-236° (decomp.).

Found %: N 5.17, 5.52. $C_{14}H_{14}NBr$. Calculated %: N 5.07.

SUMMARY

Syntheses have been carried out for the new γ-substituted piperidine alcohols, 4-(p-tolyl)- and 4-(o-tolyl)-2,5-dimethyl-4-piperidols. On the basis of these alcohols, there have been prepared 2,5-dimethyl-4-[p(o)-tolyl]-pyridines and tribasic acids of the pyridine series, 4-(p-carboxyphenyl)- and 4-(o-carboxyphenyl)-pyridine-2,5-dicarboxylic acids.

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*Original Russian pagination. See C. B. translation.

SYNTHESIS OF 2-TERT-BUTYLBUTADIENE-1,3

A. A. Korotkov, L. F. Roguleva, and V. A. Tsitokhtsev

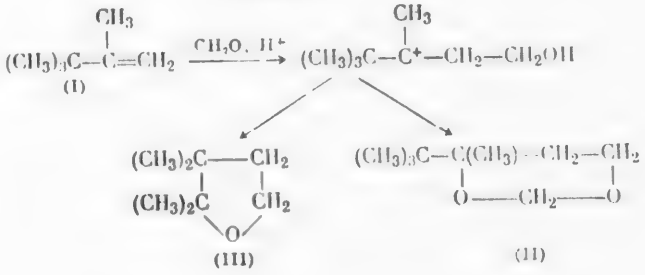
Institute of High-Molecular Compounds, Academy of Sciences of the USSR
Translated from Zhurnal Obshchei Khim., Vol. 30, No. 7, pp. 2298-2303, July, 1960
Original article submitted July 8, 1959

Various methods of synthesizing 2-tert-butyl-butadiene-1,3 are described in the literature [1-3].

The condensation reaction of olefins with aldehydes was utilized in the present work; this reaction has been used successfully for the preparation of lower dienes [4-6]. The starting materials were formaldehyde and 2,2,3-trimethylbutene-3 [1], synthesized by the Favorskii method from pinacolin [7].

The condensation of 2,2,3-trimethylbutene-3 with formaldehyde in aqueous sulfuric acid leads to the formation of 4-methyl-4-tert-butyldioxane-1,3 (II) and 2,2,3,3-tetramethyltetrahydrofuran (III), the total yield of which constitutes about 70% on the initial trimethylbutene (I) (Scheme 1).

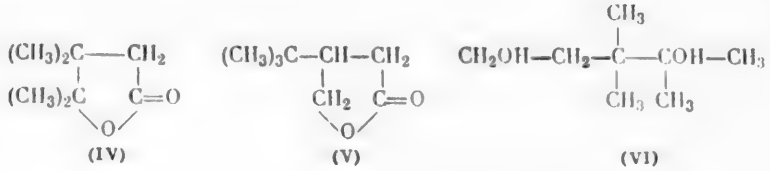
Scheme 1



The relative quantity of the dioxane decreases with increasing reaction temperature. Most of the experiments were conducted at 50-60° in 25% sulfuric acid solution.

Structures of the principal reaction products were proved in the following manner.

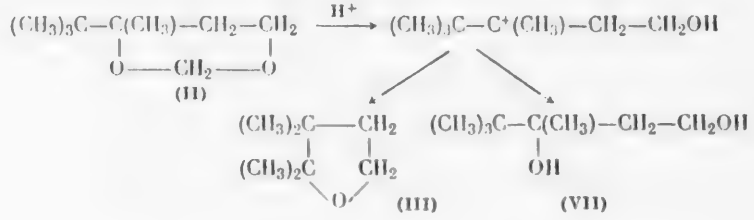
For proof of structure 2,2,3,3-tetramethyltetrahydrofuran (III) was oxidized quantitatively by aqueous permanganate solution to the γ-lactone (IV), obtained for the first time by Pechnikov [8], who incorrectly ascribed to it the formula β-tert-butyl-γ-butyrolactone (V).



Reduction of the γ-lactone (IV) by sodium in alcohol solution gives 3,3,4-trimethylpentanediol-1,4, (VI) which is esterified by phthalic anhydride [9] only at the primary hydroxyl and which gives a positive reaction for the tertiary alcohol group.

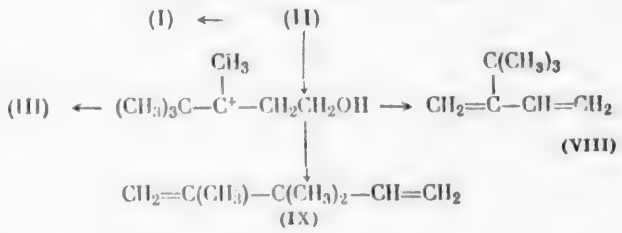
The methyl-tert-butyldioxane (II) upon hydrolysis forms 3,4,4-trimethylpentanediol-1,3 (VII); the presence of the primary and tertiary hydroxyl groups in this compound was established by the same method as that used for the glycol (VI). In addition, this hydrolysis also forms a certain quantity of tetramethyltetrahydrofuran (III), which is explained by the retropinacol rearrangement taking place upon hydrolysis of the methyl-tert-butyldioxane (II) in an acidic medium (Scheme 2). The trimethylpentanediols (VI) and (VII), while having identical elemental composition, differ in physical properties and give different derivatives with phenyl isocyanate.

Scheme 2



Conversion of the methyl-tert-butyldioxane (II) to 2-tert-butylbutadiene-1,3 (VIII) was carried out by catalytic pyrolysis on phosphate catalyst at 385-400° in the presence of water vapor. Besides the 2-tert-butylbutadiene-1,3, the pyrolysis products contained the isomeric hydrocarbon 2,3,3-trimethylpentadiene-1,4 (IX), tetramethyltetrahydrofuran (III), trimethylbutene (I), and unchanged methyl-tert-butyldioxane (Scheme 3).

Scheme 3



Trimethylpentadiene (IX) and tetramethyltetrahydrofuran (III) are formed as a result of the retropinacol rearrangement accompanying pyrolysis of the methyl-tert-butyldioxane (II). If tetramethyltetrahydrofuran (III) is passed through the contacting furnace under those same conditions, the pyrolysis is then accompanied by the pinacol rearrangement, and a mixture of the same hydrocarbons (VIII) and (IX) is formed.

The quantity of tert-butylbutadiene (VIII) in the mixture was determined by adduct formation with maleic anhydride. The unreacted trimethylpentadiene (IX) was distilled off. It was demonstrated by test with maleic anhydride that this distillate did not contain any isomer with conjugated double bonds.

The infrared spectrum of the isolated pure trimethylpentadiene (IX) showed that its bands correspond to the isopropenyl group (888 cm^{-1}) and the vinyl group (999 cm^{-1}). In addition, it was established that the ratio of isopropenyl to vinyl groups in the hydrocarbon (IX) is 1:1.

The tert-butylbutadiene (VIII) and trimethylpentadiene (IX) could not be separated successfully by fractional distillation. The highest content of tert-butylbutadiene (VIII) in the mixture of isomers was 75%. The indices of this fraction are close to those given in the literature [3] for 2-tert-butylbutadiene-1,3 (VIII), for which, however, the yield of maleic anhydride adduct was not indicated. However, our work demonstrated that the hydrocarbon distilled from the adduct does not enter into the condensation reaction with maleic anhydride and that this hydrocarbon is 2,3,3-trimethylpentadiene-1,4 (IX). Backer [1] obtained an adduct of 2-tert-butylbutadiene-1,3 with maleic anhydride with a yield of only 73% Evidently Backer [1] and also I. A. Favorskaya [2] did not obtain pure 2-tert-butylbutadiene-1,3, since they carried out the last stage of their synthesis under conditions which do not eliminate isomerization.

EXPERIMENTAL

1. Synthesis of 2,3,3-Trimethylbutene-1 (I)

A Grignard reagent was prepared from 40 g magnesium and 234 g methyl iodide in 350 ml ethyl ether; to this reagent a mixture of 150 g pinacolin and 100 ml ethyl ether was added dropwise. The pinacolin (commercially "pure" as received) was dried with sodium sulfate and distilled (b.p. 104-106°). After decomposition of the organomagnesium complex by 10% hydrochloric acid, the resulting dimethyl tert-butyl carbinol was dehydrated by distillation in the presence of iodine. The distillate was dried with calcined calcium chloride and distilled, collecting the 75-80° fraction. The yield of 2,3,3-trimethylbutene-1 was 75% relative to the pinacolin. B.p. 80°, d_0^{20} 0.7082, n_D^{20} 1.4050. These values agree with the literature data for the hydrocarbon [7].

2. Condensation of 2,3,3-Trimethylbutene-1 with Formaldehyde

150 g 2,3,3-trimethylbutene-1, 121 g formaldehyde (in the form of 32% formalin) and 114 g sulfuric acid (d 1.84) were charged to a flask with reflux condenser and stirrer. The reaction was carried out at 50-55° for 8 hours and was considered complete when the concentration of formaldehyde (determined by titration with hydroxylamine hydrochloride) became practically constant.

The organic layer was separated from the aqueous layer, then neutralized with sodium carbonate, washed with sodium sulfite and with water, dried with anhydrous sodium sulfate, and distilled. In addition to a small quantity of methylal [dimethoxymethane], the following fractions were obtained: first, 75-80°, 17 g (11.35%), initial 2,3,3-trimethylbutene-1; second, 132-136°, 50 g (25.4%); third, 64-66° (10 mm), 107.8 g (44.5%).*

a) Study of Second Fraction, B.p. 132-136°. After redistillation the material had the following constants:

B.p. 135°, m.p. 29–30°, n_D^{35} 1.4227, d_4^{35} 0.8561, MR_D 38.05; Calc. 38.51.

Found %: C 75.08, 75.26; H 12.67, 12.63. M 128.3 (cryoscopic). $C_8H_{16}O$. Calculated %: C 74.90; H 12.57. M 128.2

Oxidation of Second Fraction (B.p. 135°). 35 g of the material was oxidized by an aqueous solution of potassium permanganate (60 g) for three hours. The oxidation was carried out in a one-liter flask fitted with stirrer and reflux condenser. When the rate decreased markedly (after 2.5 hours), 10 ml of sulfuric acid (d 1.84) was added to the reaction mixture. The reaction products were extracted by ether from the acidic solution. The recovered material (38.7 g) was dissolved in a small excess of hot caustic, the solution was boiled down, and the residue was dried and washed with ethyl ether. The lactone, freed from salt by acidification, was dissolved in ether, the solution was dried with anhydrous sodium sulfate, and the ether was distilled off. M.p. 97-98°.

Found %: C 67.75, 67.94; H 9.81, 9.61. M 141.6; equiv. 143.2. $C_8H_{14}O_2$. Calculated %: C 67.57; H 9.92. M 142.2.

The analytical data and properties of the substance with m.p. 97-98° correspond to the γ-lactone (IV).

Reduction of the γ-lactone. To a solution of 10.9 g of the γ-lactone in 160 ml anhydrous alcohol, 15 g sodium was added rapidly. The solution was heated until the sodium disappeared completely. Water was added and the alcohol was steam-distilled. The glycol which was formed was extracted with ether. The glycol (2.6 g) was obtained in the form of a hygroscopic white substance melting in the range 67-77° and distilling 92° (12 mm).

Found %: C 65.82, 65.35; H 12.47, 12.10; OH 22.0, 23.2. $C_8H_{18}O_2$. Calculated %: C 65.75; H 12.33; OH 23.2.

By esterification with phthalic anhydride [9], found, %: OH 11.4, 11.2, which corresponds to one primary hydroxyl group, $C_8H_{18}O_2$.

By reaction with Deniges' reagent [10], the presence of a tertiary alcohol group in the glycol (VI) was demonstrated.

With phenyl isocyanate the glycol (VI), 3,3,4-trimethylpentanediol-1,3, forms a monourethane with m.p. 121-122°.

* The product percentages are calculated relative to the initial quantity of trimethylbutene. The trimethylbutene not accounted for in the identified products goes into a high-boiling resinous residue, which was not studied.

The experiments conducted show that the substance with b.p. 132-136° is 2,2,3,3-tetramethyltetrahydrofuran (III).

b) Study of Third Fraction with B.p. 64-66° (10 mm). The product is a colorless oily liquid.

B p. 51° (1 mm), d_4^{20} 0.9519, n_D^{20} 1.4480, MR_D 44.44; Calc. 44.85.

Found %: C 68.36, 68.35; H 11.89, 11.89. M 157.5. $C_9H_{18}O_2$. Calculated %: C 68.32; H 11.40. M 158.2.

By hydrolysis with sulfuric acid in the presence of hydroxylamine hydrochloride, the content of 4-methyl-4-tert-butyldioxane-1,3 (II) in the sample was found equal to 99.9 to 99.8%.

Hydrolysis of Methyl-tert-butyldioxane (II) by Sulfuric Acid. 30 g of the dioxane, 9 ml sulfuric acid (d 1.84) and 100 ml methanol were heated four hours on a steam bath. After neutralization with sodium carbonate, the methanol and the methylal that was formed were removed by steam distillation. The reaction products upon distillation yielded 9 g of the glycol 3,4,4-trimethylpentanediol-1,3 (VII), 6.5 g 2,2,3,3-tetramethyltetrahydrofuran (III), and 10.5 g of the unreacted dioxane (II).

3,4,4-Trimethylpentanediol-1,3, twice recrystallized from petroleum ether, appears as white lamellar crystals with m.p. 87-88°.

Found %: C 65.80, 66.09; H 12.30, 12.43; OH 22.6, 23.6; OH (primary) [9] 11.0, 11.5. $C_8H_{18}O_2$. Calculated %: C 65.75; H 12.33; OH 23.2.

The monophenylurethane of the glycol was obtained with m.p. 106-107°.

Found %: N 6.05, 5.85. $C_{15}H_{23}O_3N$. Calculated %: N 5.28.

3. Synthesis of 2-tert-Butylbutadiene-1,3 (VIII). The catalytic pyrolysis of 4-methyl-4-tert-butyldioxane-1,3 (II) and 2,2,3,3-tetramethyltetrahydrofuran (III) was carried out on acidic phosphate catalyst in a block-type electric furnace 500 mm long, having an opening for the quartz reaction tube (diameter 20 mm, length 800 mm); the reaction was conducted at 385-400° under vacuum (50 mm). Temperature was measured by a copper-constantan thermocouple. Methyl-tert-butyldioxane, tetramethyltetrahydrofuran and water in 1:1 weight ratio were fed separately from burettes. The feed rate of these products was 0.2-0.3 volumes per volume of catalyst per hour. Catalyst regeneration was performed after each experiment. The pyrolysis products were condensed in a cooler and collected in a flask chilled in ice-salt mixture. The condensate was treated with sodium bisulfite, dried, and distilled. The resulting mixture of isomeric hydrocarbons distilled in the range 100-108°.

The unsaturation of the fraction was determined by two methods: by bromide–bromate and by catalytic hydrogenation in the presence of palladium catalyst.

Iodine number, found 460, calculated for C_8H_{14}, 461. Unsaturation, determined by hydrogen absorption, 97.5% of that calculated for C_8H_{14}.

The quantitative determination of the isomeric hydrocarbons in the mixture was carried out as follows: The hydrocarbon mixture was heated one hour in a sealed ampule at 90° with a 10% excess of maleic anhydride. The unreacted trimethylpentadiene (IX) was removed by vacuum distillation. Based on the weight of the adduct with hydrocarbon (VIII) and the weight of distilled hydrocarbon (IX), the content of hydrocarbons in the mixture was determined. The adduct of 2-tert-butylbutadiene-1,3 with maleic anhydride melted at 124.5°.

Upon decomposition of the methyl-tert-butyldioxane (II), the yield of 100-108° fraction constituted 60-63% relative to the conversion of (II), the mixture containing up to 70% tert-butylbutadiene (VIII) and about 30% trimethylpentadiene (IX). Upon decomposition of the tetramethyltetrahydrofuran (III), the yield of 100-108° fraction constituted 40-45% relative to the conversion of (III), and the content of tert-butylbutadiene (VIII) in the fraction did not exceed 50%; the remainder consisted of the isomeric hydrocarbon 2,3,3-trimethylpentadiene-1,4 (IX).

Redistillation gave fractions distilling within narrower temperature ranges. The greatest quantity of 2-tert-butylbutadiene-1,3 (75%) was contained in the fraction distilling at 102-104° (760 mm); the isomeric hydrocarbon (IX) made up the other 25%.

The physicochemical indices of the 102-104° fraction: d_4^{20} 0.7434, n_D^{20} 1.4262, MR_D 38.21.

Literature data for 2-tert-butylbutadiene-1,3 (VIII): B.p. 104-106° [1]; B.p. 100–104°, $d_4^{17.5}$ 0.7304, $n_D^{17.5}$ 1.42596 [2]; B.p. 103.5-104°, d_4^{25} 0.7354, $n^{25}D$ 1.4265 [3].

The separated 2,3,3-trimethylpentadiene-1,4 has b.p. 103–104° and n_D^{20} 1.4298.

Found %: C 87.13, 87.24; H 12.99, 12.90. Iodine number 463. C_8H_{14}. Calculated %: C 87.19; H 12.35. Iodine number 461.

SUMMARY

1. A study has been made of the condensation reaction of 2,2,3 trimethylbutene-3 with formaldehyde in the presence of sulfuric acid.

2. The following compounds are described for the first time: 4-tert-butyl-4-methyldioxane-1,3; 2,2,3,3-tetramethyltetrahydrofuran; 3,3,4-trimethylpentanediol-1,4; 3,4,4-trimethylpentanediol-1,3; and 2,3,3-trimethylpentadiene-1,4.

3. It has been established that 2-tert-butylbutadiene-1,3 reacts quantitatively with maleic anhydride.

4. The structure of ββγγ-tetramethyl-γ-butylrolactone has been established.

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*Original Russian pagination. See C. B. translation.

AMINES WITH GANGLIOLYTIC ACTIVITY

III. BRANCHED-CHAIN SECONDARY DIAMINES

N. K. Kochetkov, A. Ya. Khorlin, and L. A. Vorotnikova

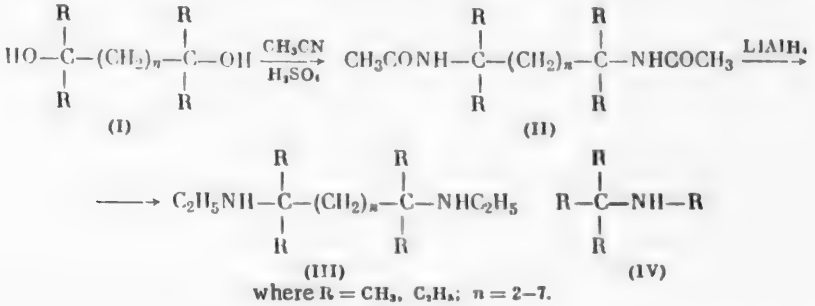
Scientific Research Institute of Pharmacology and Chemotherapy,
Academy of Medical Sciences of the USSR
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2303-2305,
July, 1960
Original article submitted September 22, 1959

In previous communications we described the synthesis of the simplest aliphatic [1] and alicyclic [2] secondary amines containing a tertiary radical and possessing strong ganglion-blocking activity. Such activity of secondary amines was discovered only very recently [3-6].

With the aim of further clarification of the dependence of pharmacological activity upon chemical structure, we undertook the synthesis of new representatives of this class of gangliolytics.

It was of particular interest to follow the change of physiological activity of branched-chain secondary diamines in comparison with monoamines (IV), since it is well known that in the case of quaternary ammonium salts the ganglion-blocking activity increases many times upon transition from the simplest salts to the bis-quaternary.

In this conclusion, in the present work there were synthesized certain secondary diamines having a quaternary carbon atom adjacent to an amino-group of a compound of Type (III). The synthesis was based on the Ritter reaction, which we had used previously for the preparation of branched monoamines [1,2,4].



where R = CH_3, C_2H_5; n = 2–7.

The physiological activity of bis-quaternary ammonium salts depends in strength and character in the first place upon the distance between the nitrogen atoms. Therefore, with the aim of investigating the analogous dependence in our compounds, we synthesized substances (III) in which the number of methylene groups (n) separating the amino groups varied from 2 to 7. In this we were limited to the synthesis of substances (III) with R = CH_3 or C_2H_5, since we had shown [1] that the greatest activity of secondary monoamines (IV) is shown in the case where the nitrogen and adjacent carbon atom carry methyl or ethyl radicals.

The initial glycols (I) were prepared from esters of the corresponding dibasic acids by the Grignard method. The previously unknown 3,10-diethyldodecanediol-3,10 was synthesized similarly by the interaction of diethyl

suberate with ethyl magnesium bromide. By interaction with acetonitrile in the presence of concentrated sulfuric acid, the substances (I) were converted to diacetyl derivatives of the corresponding diamines (II). This reaction proceeds with satisfactory yields and is the first example of utilization of the Ritter reaction for synthesis of diamines from pinacones [pinacols]. The last stage of the synthesis, reduction of the diacetyl derivatives by lithium aluminum hydride, was carried out in ether, and the diamines formed were separated in the form of the dihydrochlorides.

The synthesized diamines (III) were subjected to pharmacological assay in the Department of Private Pharmacology, Institute of Pharmacology and Chemotherapy, Academy of Medical Sciences, USSR.* All of them manifested moderate ganglion-blocking action, the greatest activity being shown by the dihydrochloride of 3,8-bis(ethylamino)-3,8-diethyldecane (III), (n = 4, R= C_2H_5). Increasing or decreasing the number n leads to a weakening of the ganglion-blocking action. Compounds (III) with R= CH_3 show less activity than Compounds (III) with R= C_2H_5.

EXPERIMENTAL

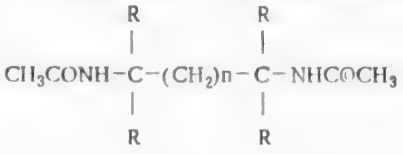
Initial Glycols (I): 3,6-Diethyloctanediol-3,6;3,8-diethyldecanediol-3,8; 3,11-diethyltridecanediol-3,11; 2,7-dimethyloctanediol-2,7; and 2,10-dimethylundecanediol-2,10 were prepared by known methods [7-10].

3,10-Diethyldodecanediol-3,10 was synthesized similarly from diethyl suberate and ethyl magnesium bromide. Yield 81%, m.p. 60-63°.

Found %: C 74.56, 74.48; H 13.11, 13.33. $C_{16}H_{34}O_2$. Calculated %: C 74.34; H 13.25.

N,N'-Diacetyl-α, ω-diaminoalkanes (II). To a mixture of 0.05 mole of glycol (I) and 0.15 mole of acetonitrile, stirred at a temperature not exceeding 40°, there was added in small portions 0.15 mole of 98% sulfuric acid. After standing two days at room temperature, the reaction mixture was poured onto ice and neutralized with 10% ammonia. The precipitated crystals were filtered off, dried, and recrystallized from ethyl acetate. Data on the N,N'-diacetyl-α,ω-diaminoalkanes obtained in this manner are shown in Table 1.

TABLE 1. N,N'-Diacetyl-α ω-diaminoalkanes (II)

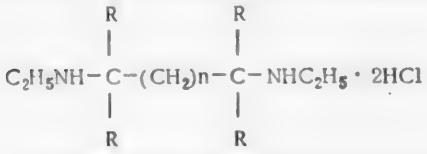


Prep. No.	R	n	Melting point	Empirical formula	% N		Yield, %
					Found	Calc.	
1	C_2H_5	2	222—223°	$C_{16}H_{32}O_2N_2$	9.90, 10.12	9.84	51.5
2	C_2H_5	4	192—193	$C_{18}H_{36}O_2N_2$	9.30, 9.32	8.97	62.4
3	C_2H_5	6	155—157	$C_{20}H_{40}O_2N_2$	7.99, 7.94	8.23	59
4	C_2H_5	7	148—149	$C_{21}H_{42}O_2N_2$	8.01, 8.00	7.9	62
5	CH_3	4	177—178	$C_{14}H_{28}O_2N_2$	10.55, 10.65	10.92	53
6	CH_3	7	121—123	$C_{17}H_{34}O_2N_2$	9.48, 9.58	9.38	60

Dihydrochlorides of N,N'-Diethyl-α,ω-diaminoalkanes (III). To a solution of 0.06 mole of lithium aluminum hydride and 50 ml of absolute ether there was added 0.01 mole of the diacyl derivative (II), and the reaction mixture was refluxed gently for 1-2 hours. Then 75 ml of 40% sodium hydroxide was added (cooling with ice), the ether layer was separated, the aqueous layer was extracted several times with ether, and the combined ether extracts were dried with solid caustic, filtered, and boiled down to a volume of 15-20 ml. Ethereal hydrogen chloride solution was then added until the hydrochloride of the diamine was completely precipitated; the latter was filtered off, washed on the filter with ether, and reprecipitated from anhydrous alcohol by ether. Data on the substances obtained are summarized in Table 2.

* The authors express deep gratitude to D. A. Kharkevich, who performed the pharmacological study of the diamines and who kindly placed at the authors' disposal the results of the assays.

TABLE 2. N,N'-Diethyl-α,ω-diaminoalkanes (III)



Prep. No	R	n	Melting point	Empirical formula	% N		% Cl		Yield, %
					Found	Calc.	Found	Calc.	
1	C_2H_5	2	276°	$C_{16}H_{38}N_2Cl_2$	8.21, 8.35	8.50	20.98, 20.99	20.92	46
2	C_2H_5	4	252—253	$C_{18}H_{42}N_2Cl_2$	7.57, 7.52	7.84	19.59, 19.44	19.84	65
3	C_2H_5	6	240—242	$C_{20}H_{46}N_2Cl_2$	7.67, 7.65	7.26	18.58, 18.66	18.39	70.4
4	C_2H_5	7	194—195	$C_{21}H_{48}N_2Cl_2$	6.74, 6.72	7.01	17.69, 17.79	17.74	50
5	CH_3	4	265	$C_{14}H_{36}N_2Cl_2$	9.63, 9.74	9.29	23.62, 23.65	23.53	71.4
6	CH_3	7	248	$C_{17}H_{40}N_2Cl_2$	8.34, 8.42	8.15	20.26, 20.34	20.61	70

SUMMARY

Synthesis has been carried out for diamines of the type $C_2H_5NHC(R)_2(CH_2)_nC(R)_2NHC_2H_5$, and the question of the dependence of their gangliolytic activity upon structure has been discussed.

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STUDIES IN THE FIELD OF QUINONES

XXXIII. CONDENSATION OF ARYLNAPHTHOQUINONES WITH SODIUM ENOLATES OF ACETOACETIC AND MALONIC ESTERS AND THEIR ANALOGS

A. N. Grinev, A. S. Mezentsev, and A. P. Terent'ev

Moscow State University
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2306-2311,
July, 1960
Original article submitted June 25, 1959

In one of our papers [1] in the instance of the reaction of aryl-1,4-naphthoquinones with sodium cyanide it was established that aryl-1,4-naphthoquinones are a convenient subject for studying the reaction of nucleophilic addition.

In the present work an investigation was made of the interaction of aryl-1,4-naphthoquinones with the sodium derivatives of acetoacetic, malonic, and benzoylacetic esters and their analogs.*

The reaction course is analogous to that of the condensation of aryl-1,4-naphthoquinones with sodium cyanide and is accompanied by a change of color of the reaction solution from yellow to dark violet, which can be explained by the formation of the phenolate of the hydroquinone. The products of the initial interaction of the sodium enolates with the arylnaphthoquinones (substituted hydroquinones) could not be isolated successfully in pure form. However, upon passing air through diluted reaction solutions, there were obtained (as a result of oxidation of the intermediate hydroquinones) substituted 2-aryl-1,4-naphthoquinones (I–VI) with the radical of the keto-enol compound substituted at position 3 of the quinone. Upon heating a reaction mixture containing the intermediate hydroquinone in a solution of acetic acid with a catalytic quantity of sulfuric acid, a derivative of 5-hydroxynaphthofuran (VII) is formed. Other derivatives of 5-hydroxynaphthofuran (VIII, IX) were obtained by the action of sulfuric acid on the hydroquinones which were formed upon reduction of the substituted arylnaphthoquinones (III, V) by sodium hydrosulfite. Under analogous conditions of treatment, the intermediate hydroquinone synthesized from 2-phenyl-1,4-naphthoquinone and sodiomalonic ester forms 2-oxo(3H)-5-hydroxy-4-phenylnaphthofuran (XI) [4-phenyl-5-hydroxynaphtho(1, 2-b)furan-2(3H)-one]. A derivative of 2-oxo(3H)-5-hydroxy-3-acetylnaphthofuran (X) was obtained in one of the experiments upon heating the intermediate hydroquinone (obtained from 2-phenyl-1,4-naphthoquinone and sodioacetoacetic ester) with aqueous caustic (Scheme 1).

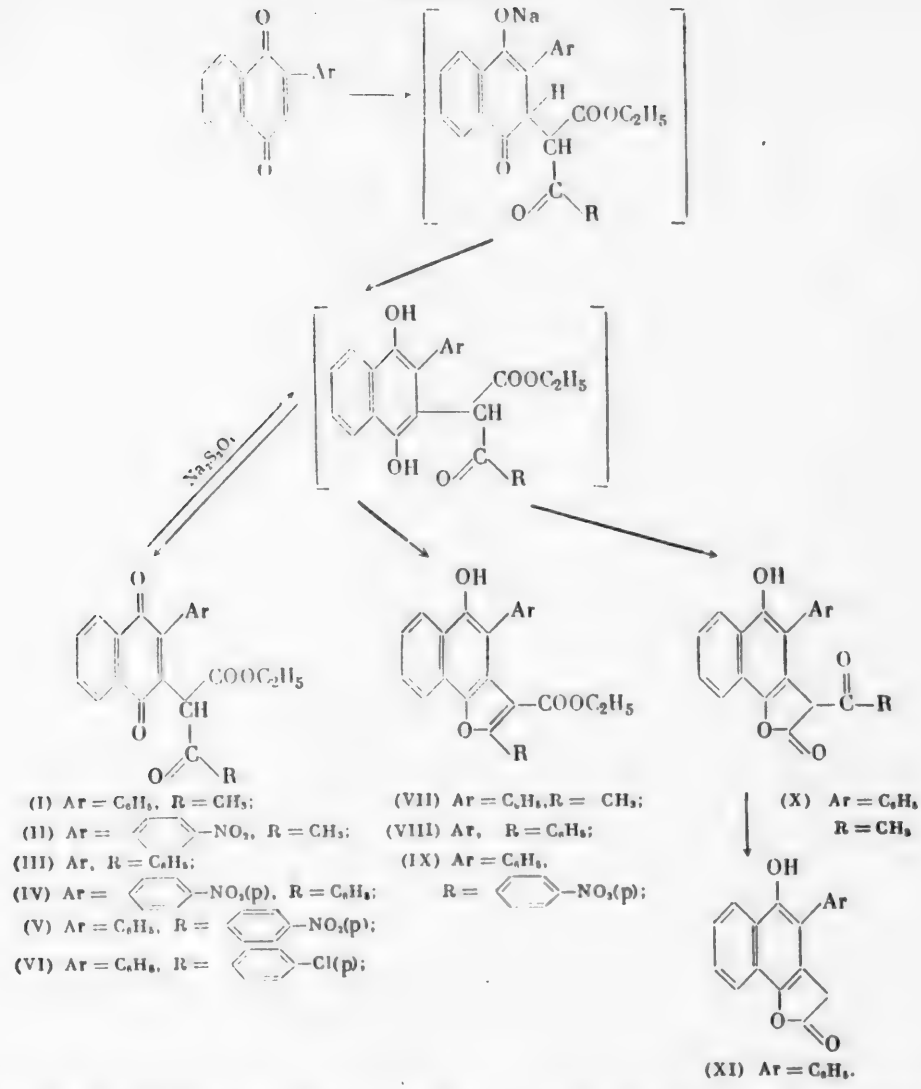
From 5-hydroxynaphthofurans (VII, VIII, IX) by the action of dimethyl sulfate there were obtained derivatives of 5-methoxynaphthofuran (XII, XIII, XIV). A 2-methyl-3-carbethoxynaphthofuran (XII) was converted through the acid (XV) to a derivative of furobenzanthracene (XVI) (Scheme 2).

EXPERIMENTAL

2-Phenyl-1,4-naphthoquinone-3-acetoacetic Ester (I). Sodioacetoacetic ester was prepared from 13 g acetoacetic ester and 2.3 g sodium in 50 ml anhydrous dioxane. To the resulting mixture there was added over one hour a solution of 23.4 g 2-phenyl-1,4-naphthoquinone in 50 ml anhydrous dioxane, cooling with ice and stirring. The reaction mixture first became dark, then acquired a violet color. After all of the 2-phenyl-1,4-naphthoquinone solution had been added, cooling was discontinued and the reaction was continued for one hour at room temperature. Then 20 ml water was added and air was passed through the solution for 1.5 hours at room temperature. The reaction solution was poured into a mixture of 300 g ice, 150 ml water, and 12 ml concentrated hydrochloric acid.

* The reaction of sodium derivatives of malonic and acetoacetic esters with p-quinones containing other substituents was studied in the works of Smith and co-authors; see for example [2-5].

Scheme 1



(I) Ar = C_6H_5, R = CH_3;
(II) Ar = $C_6H_4(NO_2)$, R = CH_3;
(III) Ar, R = C_6H_5;
(IV) Ar = $C_6H_4(NO_2)$(p), R = C_6H_5;
(V) Ar = C_6H_5, R = $C_6H_4(NO_2)$(p);
(VI) Ar = C_6H_5, R = C_6H_4Cl(p);
(VII) Ar = C_6H_5, R = CH_3;
(VIII) Ar, R = C_6H_5;
(IX) Ar = C_6H_5, R = $C_6H_4(NO_2)$(p);
(X) Ar = C_6H_5, R = CH_3
(XI) Ar = C_6H_5.

This resulted in the precipitation of a gummy mass. The aqueous layer was separated and extracted with ether. The gummy residue was treated with 100 ml ether, upon which part of the material went into solution and part remained in the form of a powdery residue. The residue was separated out, and the ether solution was combined with the ether extract of the aqueous layer and dried with magnesium sulfate. The dry solution was left to evaporate. The crystalline mass that was formed was filtered (to remove resinous admixtures) on a glass filter, washed with 15-20 ml of 50% alcohol, and dried in a vacuum desiccator over phosphorus pentoxide. Yield of the quinone (I) 12 g (30%), m.p. 118-120°. After recrystallization from methanol, m.p. 121-123°.

Found %: C 73.05, 72.99; H 5.32, 5.22. $C_{22}H_{18}O_5$. Calculated %: C 72.92; H 5.01.

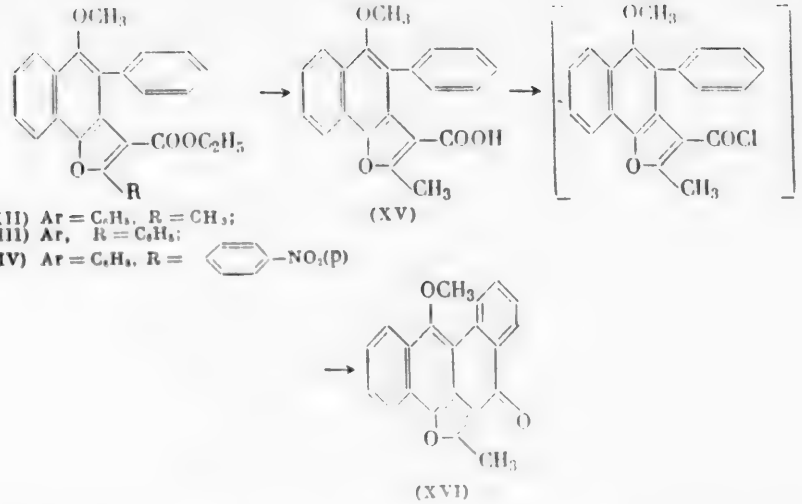
The crystalline sediment obtained after treatment of the gummy substance with ether was washed with 50% alcohol and dried in a vacuum desiccator over phosphorus pentoxide. Yield of the derivative of 2-oxo (3H)-5-hydroxynaphthofuran (X) 1.8 g (5%), m.p. 178-180°. After recrystallization from alcohol, m.p. 182–184°.

Found %: C 75.65, 75.55; H 4.52, 4.48. $C_{20}H_{14}O_4$. Calculated %: C 75.46; H 4.43.

The synthesis of other quinones substituted with the radical of a keto-enol compound was carried out similarly (see table). However, the derivative of 2-oxo (3H)-5-hydroxynaphthofuran was not detected in the other cases.

2-Methyl-3-carbethoxy-4-phenyl-5-hydroxynaphthofuran (VII). For this experiment there was taken 2.34 g 2-phenyl-1,4-naphthoquinone in 30 ml anhydrous dioxane. Sodioacetoacetic ester was prepared from 1.3 g acetoacetic ester and 0.23 g sodium in 20 ml dioxane. The condensation was conducted under the conditions of the

Scheme 2



(XII) Ar = C_6H_5, R = CH_3;
(XIII) Ar, R = C_6H_5;
(XIV) Ar = C_6H_5, R = $-NO_2(p)$

(XV)

(XVI)

previous experiment. The reaction solution was neutralized with the calculated quantity of hydrochloric acid. Then the dioxane and water were vacuum-distilled at 50-55° from the solution. The gummy residue was dissolved in 30 ml 98% acetic acid, and 3-4 drops of concentrated sulfuric acid were added to the acetic acid solution. The reaction mixture was refluxed for 1.5 hours and then diluted with an equal volume of water. The oily layer which separated was extracted with ether. The ether extract was dried with magnesium sulfate and the ether was distilled off. The resulting caramel-like mass was dried in a vacuum desiccator over sulfuric acid. Yield of (VII) 2.1 g (61%), m.p. 122-124° (from methanol).

Found %: C 76.56, 76.47; H 5.49, 5.40. $C_{22}H_{18}O_4$. Calculated %: C 76.29; H 5.23.

2,4-Diphenyl-3-carbethoxy-5-hydroxynaphthofuran (VIII). 1 g of the quinone (III) was dissolved in ether and reduced by agitating with an aqueous solution of sodium hydrosulfite (2 g). The ether layer was separated and the ether distilled off. The resulting substituted hydroquinone was dissolved in 15 ml acetic acid and 1-2 drops of concentrated sulfuric acid was added to the solution. Then the reaction and separation of the material were carried out under the conditions of the previous experiment. Yield of (VIII) 0.85 g (88%), m.p. 128-129° (from methanol).

Found %: C 79.21, 79.34; H 5.19, 4.99. $C_{27}H_{20}O_4$. Calculated %: C 79.39; H 4.94.

2-(p-Nitrophenyl)-3-carbethoxy-4-phenyl-5-hydroxynaphthofuran (IX). For experiment there was taken 1 g of the quinone (V). The synthesis was carried out under the conditions and with the quantities of substances indicated for the preceding experiment. Yield of (IX) 0.8 g (87%), m.p. 226-228° (from a 1:4 methanol–dioxane mixture).

Found %: C 71.39, 71.47; H 4.11, 4.29. $C_{27}H_{19}O_6N$. Calculated %: C 71.51; H 4.22.

2-Oxo(3H)-5-hydroxy-3-acetyl-4-phenylnaphthofuran (X). To sodioacetoacetic ester, prepared from 22 g acetoacetic ester and 3.5 sodium in 80 ml anhydrous alcohol, there was added at 0° over one hour 11.7 g of 2-phenyl-1,4-naphthoquinone in 40 ml anhydrous dioxane. Then 20 ml water was added and the solution heated one hour at 40-50°. The reaction mixture was poured onto ice and neutralized with the calculated quantity of dilute hydrochloric acid. A gummy substance was separated from the aqueous layer by decantation and was dried in a vacuum desiccator over phosphorus pentoxide. Crystals of (X) were obtained, yield 12 g (65%), m.p. 183-184° (from alcohol). A mixed sample with 2-oxo(3H)-5-hydroxy-3-acetyl-4-phenylnaphthofuran (X) obtained in one of the preceding experiments did not show any melting point depression.

2-Oxo(3H)-5-hydroxy-4-phenylnaphthofuran (XI). For the experiment there was taken 2.34 g of 2-phenyl-1,4-naphthoquinone, 1.7 g malonic ester, 0.23 g sodium, and 70 ml anhydrous dioxane. The reaction and separation of the material were carried out under the conditions of synthesis of the derivative of 5-hydroxynaphthofuran (VII). Yield of (XI) 1.3 g (50%), m.p. 195-197° (from methanol).

Found %: C 78.12, 78.23; H 4.52, 4.44. $C_{18}H_{12}O_3$. Calculated %: C 78.25; H 4.38.

Synthesis of Substituted 2-Aryl-1, 4-naphthoquinones

Starting materials	Initial quinone, g	Ester of β-keto-acid, g	Sodium, g	Dioxane, ml		Substituted 2-aryl-1, 4-naphthoquinone obtained	Yield, %	Melting point	Empirical formula	Found %		Calc. %	
				for experiment	for dissolving quinone					C	H	C	H
2-Phenyl-1, 4-naphthoquinone, acetoacetic ester	23.4	13	2.3	50	50	2-Phenyl-1,4-naphthoquinone-3-acetoacetic ester (I)	30	121 – 123° (from methanol)	$C_{22}H_{18}O_5$	73.05 72.99	5.32 5.22	72.92	5.01
2-p-Nitrophenyl-1, 4-naphthoquinone, acetoacetic ester	2.8	1.35	0.23	20	50	2-(p-Nitrophenyl)-1,4-naphthoquinone-3-acetoacetic ester (II)	52	195 – 197 (from dioxane)	$C_{22}H_{17}O_7N$	64.85 64.63	4.37 4.37	64.86	4.21
2-Phenyl-1,4-naphthoquinone, benzoylacetic ester	2.4	2	0.23	20	20	2-Phenyl-1,4-naphthoquinone-3-benzoylacetic ester (III)	40	130 – 132 (from methanol)	$C_{27}H_{20}O_5$	76.36 76.52	4.84	76.40	4.75
2-p-Nitrophenyl-1,4-naphthoquinone, benzoylacetic ester	2.8	2	0.23	20	50	2-(p-Nitrophenyl)-1,4-naphthoquinone-3-benzoylacetic ester (IV)	45	209 – 210 (from dioxane)	$C_{27}H_{19}O_7N$	69.25 69.32	4.19 4.14	69.08	4.08
2-Phenyl-1,4-naphthoquinone, p-nitrobenzoylacetic ester	2.4	2.4	0.23	30	30	2-Phenyl-1,4-naphthoquinone-3-(p-nitrobenzoylacetic) ester (V)	55	138 – 140 (from dioxane)	$C_{27}H_{19}O_7N$	68.97 69.02	4.11 4.15	69.08	4.08
2-Phenyl-1,4-naphthoquinone, p-chlorobenzoylacetic ester	2.4	2.3	0.23	30	30	2-Phenyl-1,4-naphthoquinone-3-(p-chlorobenzoylacetic) ester (VI)	37	133 – 135 (from alcohol)	$C_{27}H_{19}O_5Cl$	70.66 70.51	4.39 4.36	70.64	4.17

2-Methyl-3-carbethoxy-4-phenyl-5-methoxynaphthofuran (VII). To a solution of 0.5 g of the 5-hydroxynaphthofuran (VII) and 10 ml dioxane there was added 10 ml 2 N sodium hydroxide solution and 1 ml dimethyl sulfate. The reaction mixture was agitated for one hour in a closed container at room temperature, then diluted with an equal volume of water. The precipitate was filtered off, washed with water, and dried in a vacuum desiccator over phosphorus pentoxide. Yield of (XII) 3.4 g (95%), m.p. 122-123° (from methanol).

Found %: C 76.71, 76.83; H 5.70, 5.79. $C_{23}H_{20}O_4$. Calculated %: C 76.66; H 5.59.

2,4-Diphenyl-3-carbethoxy-5-methoxynaphthofuran (XIII). For experiment there was taken 0.82 g of the 5-hydroxynaphthofuran (VIII), 0.5 g dimethyl sulfate, 2 ml 2 N sodium hydroxide solution, and 2 ml dioxane. The reaction and separation of the material were carried out under the conditions of the preceding experiment. Yield of (XIII) 0.8 g (91%), m.p. 106-107° (from methanol).

Found %: C 79.70, 79.66; H 5.46, 5.37. $C_{28}H_{22}O_4$. Calculated %: C 79.60; H 5.25.

2-(p-Nitrophenyl)-3-carbethoxy-4-phenyl-5-methoxynaphthofuran (XIV). For experiment there was taken 0.45 g of the 5-hydroxynaphthofuran (IX), 0.25 g dimethyl sulfate, 1 ml 2 N sodium hydroxide solution, and 1 ml dioxane. The reaction and separation of material were carried out as previously. Yield of (XIV) 0.4 g (87%), m.p. 201-202° (from 1:4 methanol–dioxane mixture).

Found %: C 71.76, 72.06; H 4.58, 4.67. $C_{28}H_{21}O_6N$. Calculated %: C 71.94; H 4.53.

2-Methyl-3-carboxy-4-phenyl-5-methoxynaphthofuran (XV). 3.6 g of (XII) was refluxed four hours with alcoholic caustic, prepared from 2 g sodium hydroxide and 50 ml alcohol. Then the reaction mixture was diluted with two volumes of water and the ester (XII) was filtered off. From the filtrate, the alcohol was distilled off and the acid (XV) was recovered upon acidification with hydrochloric acid (to acidic reaction with Congo red). Yield of (XV) 2 g, m.p. 214-216° (from 60% acetic acid).

Found %: C 75.81, 75.98; H 4.97, 5.01. $C_{21}H_{16}O_4$. Calculated %: C 75.89; H 4.85.

5-Oxo-6-methyl-12-methoxy-5-p-furo(2,3,4 g h)-benz-(1,2 a)-anthracene (XVI). To a solution of 3 g thionyl chloride in 30 ml carbon tetrachloride there was added 1.6 g of the acid (XV); the resulting suspension was heated to 40° and stirred until all of the acid (XV) dissolved. The solution was cooled to 0° and there was added to it in small portions a suspension of 1.4 g aluminum chloride in 20 ml carbon tetrachloride. Then the reaction mixture was held one hour at 0° and three hours at room temperature. The reaction solution was poured into a mixture of 100 ml water and 100 g ice, and dilute hydrochloric acid was added up to acidic reaction with Congo red. The carbon tetrachloride layer was separated and washed several times with water and with sodium carbonate solution. The solution of the ketone (XVI) in carbon tetrachloride was dried with magnesium sulfate and the solvent was removed by vacuum distillation. The dry residue was recrystallized from methanol.* Yield of ketone 0.5 g, m.p. 174-176° (after two recrystallizations from methanol).

Found %: C 79.63, 79.83; H 4.58, 4.39. $C_{21}H_{14}O_3$. Calculated %: C 80.24; H 4.49.

SUMMARY

1. A study has been made of the reaction of aryl-1,4-naphthoquinones with sodium derivatives of acetoacetic and malonic esters and their analogs. On the basis of this reaction a preparative method has been developed for the synthesis of 2-aryl-1,4-naphthoquinones substituted in the 3-position by the radical of the keto-enol compound.

2. It has been shown that the substituted hydroquinones obtained as a result of the interaction of arylnaphthoquinones with sodium acetoacetic ester and its analogs, or by reduction of the corresponding quinones, are readily converted to derivatives of 5-hydroxynaphthofuran and 2-oxo(3H)-5-hydroxynaphthofuran.

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*In the recrystallization process, 0.9 g of the initial acid (XV) was recovered.

**Original Russian pagination. See C. B. translation.

RESEARCHES ON QUINONES

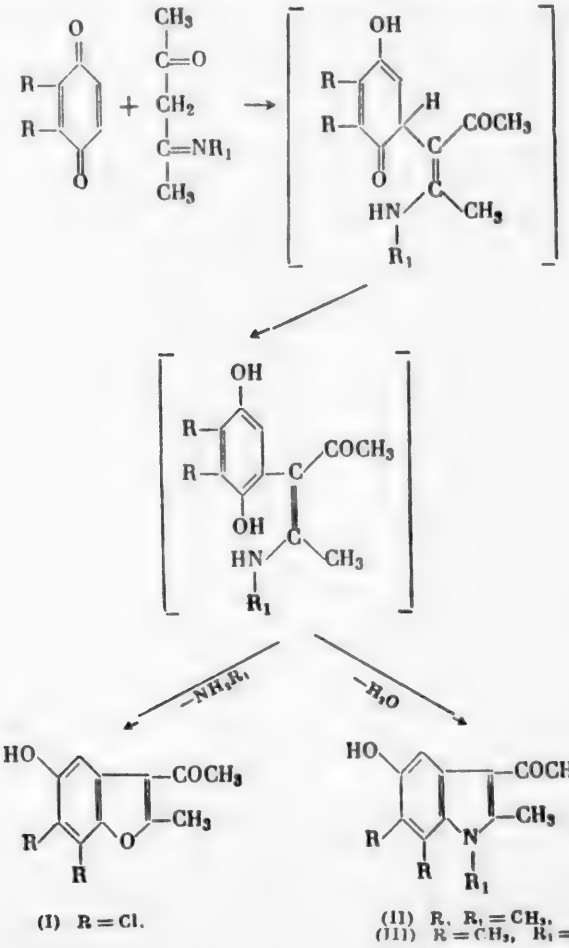
XXXIV. CONDENSATION OF p-QUINONES WITH IMINES OF ACETYLACETONE

A. N. Grinev, V. L. Florent'ev, V. I. Shvedov, and A. P. Terent'ev

Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2311-2315,
July, 1960
Original article submitted June 25, 1959

In previous papers we showed that p-benzoquinone reacts with an imine of acetylacetone to give a mixture of 2-methyl-3-acetyl-5-hydroxyindole and 2-methyl-3-acetyl-5-hydroxybenzofuran [1], and that p-benzoquinone with N-alkyl imines of acetylacetone gives derivatives of benzofuran [2]. Condensation of p-benzoquinone with an N-phenylimine of acetylacetone gives only a derivative of 5-hydroxyindole [3].



(I) R = Cl.

(II) R, $R_1 = CH_3$.
(III) R = CH_3, $R_1 = C_6H_5$.

TABLE 1. Condensation of p-Quinones with Acetylacetone Imines

Starting materials	Quinone (in g)	Imine (in g)	Dichloroethane (in ml) for dissolving		Products	Yield (%)	Melting point		Empirical formula	Found %		Calculated	
			imine	Quinone			found	literature		C	H	C	H
2,3-Dichloro-p-benzoquinone, acetylacetone N-methylimine	1.8	1.4	5	25	2-Methyl-2-acetyl-5-hydroxy-6,7-dichlorobenzofuran (I)	74	260–261°	260.5° [5]	$C_{11}H_8O_2Cl_2$	–	–	–	–
2,3-Dichloro-p-benzoquinone, acetylacetone N-phenylimine	1.8	2.25	5	25	2-Methyl-3-acetyl-5-hydroxy-6,7-dichlorobenzofuran (I)	99	261–262	260.5 [5]	$C_{11}H_8O_2Cl_2$	51.02 51.14	3.09 3.16	50.99	3.11
o-Xyloquinone, acetylacetone N-methylimine	2.72	2.8	10	50	1,2,6,7-Tetramethyl-3-acetyl-5-hydroxyindole (II)	28	276–277 (from dioxane)	–	$C_{14}H_{17}O_2N$	72.67 72.89	7.44 7.52	72.70	7.41
o-Xyloquinone*, acetylacetone N phenylimine	2.72	4.5	10	50	1-Phenyl-2,6,7-trimethyl-3-acetyl-5-hydroxyindole (III)	45	285–286 (from dioxane)	–	$C_{19}H_{19}O_2N$	77.60 77.68	6.62 6.60	77.79	6.53
α-Naphthoquinone, acetylacetone N-methylimine	6.4	5.7	20	100	1,2-Dimethyl-3-acetyl-5-hydroxybenzindole (IV),	Total Yield 74**	316–318	–	$C_{16}H_{15}O_2N$	75.88 75.76	5.92 6.04	75.86	5.96
					2-methyl-3-acetyl-5-hydroxynaphthofuran (V)		263–264	262 [6]	$C_{15}H_{12}O_3$	–	–	–	–
α-Naphthoquinone, acetylacetone N-phenylimine	15.8	22	20	250	1-Phenyl-2-methyl-3-acetyl-5-hydroxybenzindole (VI)	69	309–311 (from dioxane)	–	$C_{12}H_{17}O_2N$	79.90 79.78	5.62 5.62	79.97	5.43

*In this experiment the reaction flask was heated over a gas burner.

**The substances were separated by fractional crystallization from dioxane.

TABLE 2. Synthesis of Derivatives of 5-Methoxybenzofuran, 5-Methoxyindole, 5-Methoxynaphthofuran and 5-Methoxybenzindole

Starting materials		Dimethyl-sulfate (in g)	2N NaOH (in ml)	Dioxane (in ml)	Products	Yield (%)	Melting point		Empirical formula	Found	Calc.
No. in text	Quantity (in g)						Found	Literature values		N	N
(I)	2.6	2.5	10	8	2-Methyl-3-acetyl-5-methoxy-6, 7-dichlorobenzofuran (VIII)	97	187—188° from methanol	188° [5]	$C_{12}H_{10}O_2Cl_2$	—	—
(II)	0.6	0.66	2.6	6	1,2,6,7-Tetramethyl-3-acetyl-5-methoxyindole (IX)	98	155—156 from methanol	—	$C_{12}H_{10}O_2Cl_2$	5.62, 5.65	5.71
(III)	0.4	0.35	1.4	4	1-Phenyl-2, 6,7-trimethyl-3-acetyl-5-methoxyindole (X)	93	189—190 from methanol	—	$C_{20}H_{21}O_2N$	4.74, 4.67	4.56
(IV)	0.3	0.3	1.2	2	1,2-Dimethyl-3-acetyl-5-methoxybenzindole (XI)	94	190—191 from methanol	—	$C_{17}H_{17}O_2N$	5.53, 5.45	5.24
(V)	0.24	0.25	1	2	2-Methyl-3-acetyl-5-methoxynaphthofuran (XII)	90	184—185 from methanol	183—184 [6]	$C_{16}H_{14}O_3$	—	—
(VI)	5.9	4.9	19	20	1-Phenyl-2-methyl-3-acetyl-5-methoxybenzindole (XIII)	98	163—164 from methanol	—	$C_{22}H_{19}O_2N$	4.32, 4.14	4.25

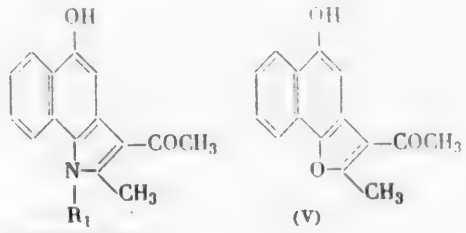
These results may be explained, as shown in the scheme presented in our paper [1], by the tendency of the intermediate hydroquinones to enolize in two directions.

The present study concerns the reaction of N-methyl-and N-phenylimines of acetylacetone with substituted p-quinones—o-xyloquinone, 2,3-dichloroquinone, and also α-naphthoquinone, and it was shown that, depending upon the nature of the substituent in the quinone nucleus, either a derivative of benzofuran (I) or substituted indoles (II, III) are formed (see scheme above).

If the intermediate hydroquinone contains negative substituents (R = Cl), then the reaction is independent of the nature of the substituent on the imine nitrogen and a benzofuran (I) is formed. If the substituents in the intermediate hydroquinone enrich the nucleus with electrons (R = CH_3), the strength of the carbon-oxygen bond is decreased. In this case water is split off and derivatives of indole (II, III) are obtained.

Condensation of α-naphthoquinone with acetylacetone N-methylimine gave a mixture of 1,2-dimethyl-3-acetyl-5-hydroxybenzindole (IV) and 2-methyl-3-acetyl-5-hydroxynaphthofuran (V), but when α-naphthoquinone was reacted with acetylacetone N-phenylimine only a derivative of indole (VI) was obtained.

Consequently, the direction of the condensation reaction between p-quinones and acetylacetone imines depends upon the nature of the substituents in the quinone nucleus and on the imine nitrogen.



(IV) $R_1 = CH_3$.
(VI) $R_1 = C_6H_5$.

(V)

In the present study we found the optimum conditions for the reaction between p-benzoquinone and acetylacetone N-phenylimine; 1-phenyl-2-methyl-3-acetyl-5-hydroxyindole (VII) was obtained in a yield of 53%. Condensations of other p-quinones with imines of acetylacetone were carried out under the conditions used for reacting p-benzoquinone with acetylacetone N-phenylimine.

All the derivatives obtained of 5-hydroxybenzofuran (I), 5-hydroxyindole (II, III), 5-hydroxynaphthofuran (V), and 5-hydroxybenzindole (IV, VI) were treated with dimethyl sulfate to give the corresponding 5-methoxy derivatives (VIII-XIII). The methylation was carried out under conditions described in one of our previous papers [4].

EXPERIMENTAL

1-Phenyl-2-methyl-3-acetyl-5-hydroxyindole (VII). A mixture of 44.7 g of acetylacetone N-phenylimine and 100 ml of dichloroethane was placed in a Wurtz flask. The resulting solution was heated on a water bath, and to it was added a solution of 21.6 g of p-benzoquinone in 500 ml of dichloroethane in the course of 1.5 hours by means of a dropping funnel. During this process dichloroethane distilled off as an azeotropic mixture with water, and 560-580 ml of the azeotrope was collected in 2 hours. The residue was cooled in a refrigerator, and the crystals which formed were filtered off and washed with ether. The yield of indole (VII) was 28.6 g (53%) with m.p. 233-234° (from dioxane); the literature gives the m.p. as 232-233° [3].

Condensation of other p-quinones with acetylacetone imines was carried out in a similar way (see Table 1). The products were methylated as described in one of our papers [4], and the results are presented in Table 2.

SUMMARY

The reaction between p-quinones and acetylacetone imines was studied. It was shown that this reaction follows different courses depending upon the nature of the substituents in the quinone nucleus and on the imine nitrogen, with the result that either derivatives of indole or substituted benzofurans are formed.

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STUDIES IN THE FIELD OF THE QUINONES

XXXV. THE BROMINATION OF THE "ACID COMPLEX" OF p-BENZOQUINONE BY THE METHOD OF CHELINTSEV

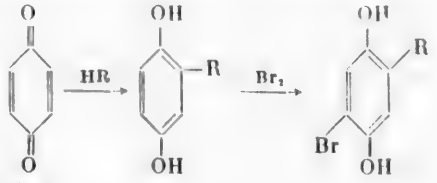
A. N. Grinev, V. L. Florent'ev, and A. P. Terent'ev

Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2316-2317, July, 1960
Original article submitted June 25, 1959

V. V. Chelintsev [1] when brominating the "acid complexes" formed by solution of p-benzoquinone in excess concentrated hydrochloric and hydrobromic acids obtained a product of addition of bromine to p-benzoquinone dibromide. We wished to use this compound for preparation of 2,3-dibromo-p-benzoquinone.

When we repeated the synthesis of the quinone dibromide under the conditions and with the amounts of substances reported in the work of V. V. Chelintsev [1], we obtained in the bromination of p-benzoquinone in hydrochloric acid 2-chloro-5-bromohydroquinone, and when we carried out the reaction in hydrobromic acid, we obtained 2,5-dibromohydroquinone. Hence, the bromination of p-benzoquinone in solutions of hydrochloric and hydrobromic acids occurs through the stage of formation of chlorobromohydroquinone by the usual scheme.



R = Cl, Br.

As a result of the oxidation of 2-chloro-5-bromohydroquinone and 2,5-dibromohydroquinone by potassium bromate we obtained 2-chloro-5-bromo-p-benzoquinone and 2,5-dibromo-p-benzoquinone.

EXPERIMENTAL

2-Chloro-bromohydroquinone. We dissolved 10.8 g of p-benzoquinone in 135 ml of concentrated hydrochloric acid. To the resulting solution, with stirring, we added 16 g of bromine dropwise. The resulting precipitate was filtered off and washed with water. Yield of 2-chloro-5-bromohydroquinone 17.7 g (80%), m.p. 170-171° (from aqueous methanol). According to the literature [2], m.p. 171-172°.

2,5-Dibromohydroquinone. From 10.8 g of p-benzoquinone and 16 g of bromine in 170 ml of concentrated hydrobromic acid under the conditions of the previous experiment we obtained 20 g (75%) of 2,5-dibromohydroquinone with m.p. 185-186° (from aqueous methanol). According to the literature [3], m.p. 186°.

2-Chloro-5-bromo-p-benzoquinone. We dissolved 2.23 g of 2-chloro-5-bromohydroquinone in 10 ml of dioxane. To the resulting solution, with stirring, we added 1.5 ml of 1 N sulfuric acid and 1.7 g of potassium bromate in 17 ml of water. The reaction temperature of the mixture was kept at 50-60°. The precipitate of the quinone was filtered off and washed with water. Yield of 2-chloro-5-bromo-p-benzoquinone 2.1 g (96%), m.p. 174-175° (from methanol). According to the literature [2], m.p. 175°.

2,5-Dibromo-p-benzoquinone. Under the conditions of the previous experiment we obtained from 4.1 g of 2,5-dibromo-p-benzoquinone with m.p. 188-189° (from methanol). According to the literature [4], m.p. 188°.

SUMMARY

We have showed that in the bromination of p-benzoquinone in solutions of hydrochloric and hydrobromic acids by the method of Chelintsev there is formed not a quinone dibromide, but 2-chloro-5-bromohydroquinone and 2,5-dibromohydroquinone.

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ORGANIC INSECTOFUNGICIDES

LV. THE SYNTHESIS OF SOME ALKYL ARYL THIOPHOSPHORIC ACID HYDRAZIDES

A. G. Zen'kevich, P. G. Zaks, Ya. A. Mandel'baum,

and N. N. Mel'nikov

Scientific Institute for Fertilizers and Insectofungicides, Moscow

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2317-2319, July, 1960
Original article submitted July 6, 1959

In our laboratory we have recently synthesized a number of substituted amides and hydrazides of dialkythiophosphoric acid [1], some of which were found to be sufficiently active systemic insecticides [2]. In connection with the study of the relation between structure and insecticidal activity of organic phosphorus compounds and the search for new active insecticides it seemed interesting to synthesize the hydrazides of alkyl aryl thiophosphoric acids also, since in many cases the replacement of an aliphatic radical by an aromatic one in different derivatives of thiophosphoric acid leads to a considerable change in insecticidal properties.

The synthesis of hydrazides of alkyl aryl thiophosphoric acids was carried out by the reaction which we have recently described of alkyl aryl chlorothiophosphates [3] with hydrazine hydrate and phenylhydrazine in ether.

$$\begin{matrix} RO \\ ArO \end{matrix}\!\!>\!PSCl + 2NH_2{-}NHR' \longrightarrow \begin{matrix} RO \\ ArO \end{matrix}\!\!>\!PSNH{-}NHR' + R'NH{-}NH_2 \cdot HCl\,.$$

This reaction takes place very easily and the corresponding hydrazides are formed in good yields. The compounds which we obtained and their properties are given in the table. Most of the compounds which we synthesized are not described in the literature, and only two of them have very recently been described in patents [4, 5]. Study of these synthesized compounds as contact insecticides was carried out by P. V. Popov and S. A. Roslavtseva on rice weevils and showed that they had very weak activity.

EXPERIMENTAL

In a flask with reflux condenser, dropping funnel, and mechanical stirrer with a seal we placed a solution of the alkyl aryl chlorothiophosphate (0.1 mole) in 200 ml of ether, and we added gradually with good stirring hydrazine hydrate of phenylhydrazine (0.2 mole). Addition of hydrazine was carried out at 20° and the temperature then fell 3-7°. After addition of the hydrazine, the reaction mass was kept at 20° for 2-4 hours and at 35° for two hours. Then the reaction mixture was washed with water to remove hydrazine hydrochloride, the ether solution was dried and the ether was distilled off on the water bath. The crystalline residue was purified by recrystallization from ether, ligroin, or alcohol or mixtures of these solvents. The resulting compounds and their properties are given in the table.

SUMMARY

In order to study the relation between structure and insecticidal activity of different derivatives of thiophosphoric acid and to search for new insecticides, we synthesized a series of undescribed hydrazides and phenyl-

hydrazides of alkyl aryl thiophosphoric acids. All the compounds synthesized were very weak contact insecticides.

Properties of Alkyl Aryl Thiophosphoric Acid Hydrazides

Formula	Yield, %	M. p.	% P		% N	
			Found	Calc.	Found	Calculated
C_6H_5O, CH_3O >PSNH–NH_2*	78	—	14.15, 13.66	14.20	12.44	12.83
C_6H_5O, C_2H_5O >PSNH–NH_2**	85	—	13.28	13.26	11.64	12.07
(4) $O_2NC_6H_4O$, CH_3O >PSNH–NH_2	68	100°	11.65	11.78	15.99, 15.88	15.96
(4) $O_2NC_6H_4O$, C_2H_5O >PSNH–NH_2	63	80	11.25	11.20	15.20, 15.27	15.16
(4) $O_2NC_6H_4OPS(NH–NH_2)_2$	90	142	11.26	11.78	26.65	26.66
2,4-$Cl_2C_6H_3O$, C_2H_5O >PSNH–NH_2***	91	—	10.16	10.30	9.34, 9.13	9.30
C_6H_5O, CH_3O >PSNH–NHC_6H_5	42	80	10.86	10.82	9.37, 9.24	9.52
C_6H_5O, C_2H_5O >PSNH–NHC_6H_5	35	57	10.60	10.05	9.09, 8.80	9.09
(4) $O_2NC_6H_4O$, CH_3O >PSNH–NHC_6H_5	73	125—127	9.30	9.15	12.29, 12.23	12.39
(4) $O_2NC_6H_4O$, C_2H_5O >PSNH–NHC_6H_5	65	68	9.30	8.80	12.00, 12.01	11.90
2,4,5-$Cl_3C_6H_2O$, C_2H_5O >PSNH–NHC_6H_5	59	108—110	7.30	7.54	7.30	6.82
2,4-$Cl_2C_6H_3O$, C_2H_5O >PSNH–NHC_6H_5	81	62	7.90	8.22	7.60	7.43
(4) $O_2NC_6H_4OPS(NH–NHC_6H_5)_2$	87	176	7.01	7.47	16.73, 16.55	16.86

*Does not distill at 0.01 mm. After distillation of the light fraction in a high vacuum, d_4^{20} 1.3114, n_D^{20} 1.5875.

**B. p. 147-150° (0.3 mm), d_4^{20} 1.2242, n_D^{20} 1.5600.

***Does not distill without decomposition at 0.01 mm. After distillation of the light fraction in a high vacuum, d_4^{20} 1.4174, n_D^{20} 1.5852.

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*Original Russian pagination. See C. B. translation.

ORGANIC INSECTOFUNGICIDES

LVI. THE REACTION OF BIS(DIALKOXYTHIOPHOSPHONIUM)-DISULFIDES WITH TRIARYL- AND DIARYLPHOSPHITES

N. N. Mel'nikov, K. D. Shvetsova-Shilovskaya, and M. Ya. Kagan

Scientific Institute for Fertilizers and Insectofungicides, Moscow

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2319-2322,
July, 1960
Original article submitted July 11, 1959

We recently showed [1] that in the reaction of trialkylphosphites with bis(dialkoxythiophosphonium)-disulfides we obtained good yields of trialkyldithiophosphates and tetraalkyldithiopyrophosphates, whose formation evidently occurs through the Arbuzov rearrangement. The reaction of trialkylphosphites with some other disulfides [2-4] and thiocyanates [5,6] proceeds in an analogous way. However, in one case there occurs formation of thiolphosphates and in the other of thionephosphates. When we analyze the existing material we can conclude that thionephosphates are obtained in those cases where the original trialkylphosphite contains a comparatively high-molecular-weight ester group with slight mobility, and especially with aromatic radicals, since in esters the latter are less easily replaced by other groups. In order to confirm this idea, we felt it would be interesting to study the reaction of bis(dialkoxythiophosphonium)-disulfides with triarylphosphites since because of the slight ability to migrate of aromatic radicals in the case mentioned we should obtain practically only triarylthiophosphates and tetraalkyltrithiopyrophosphates.

As a result of carrying out the reaction we succeeded in showing that the reaction of triarylphosphites with bis(dialkoxythiophosphonium) disulfides occurs almost entirely by scheme (1) and forms good yields of triarylthiophosphates and tetraalkyltrithiopyrophosphates:

$$[(RO)_2P(S)]_2S_2 + (ArO)_3P \longrightarrow (RO)_2\overset{\overset{S}{\|}}{P}-S-\overset{\overset{S}{\|}}{P}(OR)_2 + (ArO)_3PS. \quad (1)$$

Evidently there first occurs formation of unstable addition products which are then decomposed according to scheme (2)

$$(ArO)_3P\begin{matrix}SP(S)(OR)_2\\SP(S)(OR)_2\end{matrix} \longrightarrow (RO)_2\overset{\overset{S}{\|}}{P}-S-\overset{\overset{S}{\|}}{P}-(OR)_2 + (ArO)_3PS. \quad (2)$$

In the case of trialkylphosphites, decomposition occurs according to scheme (3).

$$(R'O)_3P\begin{matrix}SP(S)(OR)_2\\SP(S)(OR)_2\end{matrix} \longrightarrow (RO)_2\overset{\overset{S}{\|}}{P}-S-\overset{\overset{O}{\|}}{P}(OR')_2 + (RO)_2\overset{\overset{S}{\|}}{P}-SR'. \quad (3)$$

The reaction of triarylphosphites with bis(dialkoxythiophosphonium)-disulfides is a good process for obtaining tetraalkyltrithiopyrophosphates. The compounds which we obtained and their properties are given in the table.

Properties of Reaction Products of bis (Dialkoxythiophosphonium)-disulfides with Triarylphosphites

Formulas of starting compounds	Formulas of compounds obtained	Yield, %	B. p. (pressure in mm)	M.p.	Found	Empirical formula	Calc.
$[(CH_3O)_2P(S)S]_2$ $(C_6H_5O)_3P$	$(CH_3O)_2PSSSP(O)CH_3)_2$ $(C_6H_5O)_3PS$	78 74	108.5—111°(0.07) 155—160 (0.15)	34° 49	21.58, 22.01 —	$C_4H_{12}O_4S_3P_2$ —	21.90 —
$[(C_2H_5O)_2P(S)S]_2$ $(C_6H_5O)_3P$	$[(C_2H_5O)_2P(S)]_2S$ $(C_6H_5O)_3PS$	69 63	— — — —	41* 49	18.40, 18.00 —	$C_8H_{20}O_4S_3P_2$ —	18.36 —
$[(iso\text{-}C_3H_7O)_2P(S)S]_2$ $(C_6H_5O)_3P$	$[(iso\text{-}C_3H_7O)_2P(S)]_2S$ $(C_6H_5O)_3PS$	86 84	107—108 (0.08) 160—162 (0.08)	— 49	15.75, 15.59 9.06, 8.89	$C_{12}H_{28}O_4S_3P_2$ $C_{18}H_{15}O_3SP$	15.70 9.04
$[(C_2H_5O)_2P(S)S]_2$ $(4\text{-}ClC_6H_4O)_3P$	$[(C_2H_5O)_2P(S)]_2S$ $(4\text{-}ClC_6H_4O)_3PS$	48 49	105—112 (0.05) 190—200 (0.15)	40 108.5**	18.39, 18.44 6.84, 6.91	$C_8H_{20}O_4S_3P_2$ $C_{18}H_{12}O_3Cl_3SP$	18.36 6.95
$[(iso\text{-}C_3H_7O)_2P(S)S]_2$ $(4\text{-}ClC_6H_4O)_3P$	$[(iso\text{-}C_3H_7O)_2P(S)]_2S$ $(4\text{-}ClC_6H_4O)_3PS$	40 74	126—129 (0.25) 190—200 (0.15)	— 108	15.56, 15.88 —	$C_{12}H_{28}O_4S_3P_2$ —	15.70 —

* According to [12], m. p. 41-42°

** According to [13], m. p. 85-86°, and according to [14], 113°

In order to confirm our results by another example we also studied the reaction of bis(dialkoxythiophosphonium)-disulfides with diarylphosphites. As expected, the reaction of bis(dialkoxythiophosphonium)-disulfides with diarylphosphites occurs by a different path than with dialkylphosphites. If the chief product in the reaction with dialkylphosphites is trialkyldithiophosphate (I), with diarylphosphites, bis(dialkoxythiophosphonium) disulfide gives tetraalkyltrithiopyrophosphates and salts of dialkyldithiophosphoric acid. In its general form this reaction can be represented by scheme (4).

$$[(RO)_2P(S)]_2S_2 + (ArO)_2PONa \longrightarrow (RO)_2P(=S)-S-P(=S)(OR)_2 +$$
$$+ (RO)_2P(=S)-SNa + \left[(ArO)_2P(=O)-O-P(=S)(OAr)_2\right]$$
$$\left[(ArO)_2P(=O)-O-P(=S)(OAr)_2\right] \longrightarrow (ArO)_3P{=}S + ArO-P(=O)(=O) \qquad (4)$$

The formation of triarylthiophosphates can be explained by a disproportionation reaction, which is often found for esters of acids of phosphorus [7].

EXPERIMENTAL

1. Reaction of triarylphosphites with bis(dialkoxythiophosphonium)-disulfides. In a flask with a reflux condenser, mechanical stirrer, and dropping funnel was placed 8.5 g of bis(diisopropyloxythiophosphonium)-disulfide and 30 ml of anhydrous benzene. To the resulting solution was gradually added 6.2 g of triphenylphosphite. The temperature increased by 10-15°. Then the reaction mixture was boiled for three hours on a water bath. After the reaction had ended the benzene was distilled off and the residue was distilled in a vacuum. We obtained two fractions: the first with b.p. 107-108° (0.08 mm), d_4^{20} 1.1081, n_D^{20} 1.5120. Yield 6.8 g (86%).

Found %: P 15.75, 15.59. $C_{12}H_{28}O_4P_2S_3$. Calculated %: P 15.70.

The second fraction had b.p. 160-162° (0.08 mm), m.p. 48-49° (from anhydrous alcohol). Yield 5.75 g (84%).

Found %: P 9.09, 8.89. $C_{18}H_{15}O_3PS$. Calculated %: P 9.04.

According to [8,9], triphenylthiophosphate has m.p. 48°.

Under exactly the same conditions we carried out the reaction with the other compounds; the results of these experiments are given in the table.

2. Reaction of bis(dialkoxythiophosphonium)-disulfide with diphenylphosphite. The required diphenylphosphite was obtained by the method of [10]. To 7 g of freshly distilled diphenylphosphite in 30 ml of benzene was added 0.66 g of metallic sodium, and the reaction mixture was boiled in a flask with a reflux condenser until all the sodium had been converted into the salt of diphenylphosphorous acid (1-1.5 hours), and then the reaction mixture was treated with 7.8 g of bis(dimethoxythiophosphonium)-disulfide in 20 ml of anhydrous benzene at 40-50°. The reaction mixture was boiled for three hours under reflux with good stirring. At the end of the reaction the precipitate was filtered (4.6 g), the benzene was distilled off, and the residue was fractionated in a vacuum.

We obtained two fractions.

The first, tetramethyltrithiopyrophosphate, b.p. 114-115° (0.1 mm). Yield 3.25 g (92%), d_4^{20} 1.3321, m.p. 33-34°.

Found %: P 21.20, 21.07. $C_4H_{12}O_4P_2S_3$. Calculated %: P 21.95.

The second, triphenylthiophosphate, b.p. 148-152° (0.05 mm), m.p. 48-49°. A sample mixed with pure triphenylthiophosphate obtained by another method gave no depression of the melting point. The yield was practically quantitative.

Found %: P 9.30, 9.36. $C_{18}H_{15}O_3PS$. Calculated %: P 9.04.

The precipitate, washed with benzene, was dissolved in water and treated with an aqueous solution of lead

salt of dimethyldithiophosphoric acid. After the salt had been recrystallized from alcohol, it melted at 123-123°. A sample mixed with pure lead salt of dimethyldithiophosphoric acid obtained from sodium dimethyldithiophosphate gave no melting point depression.

Found %: C 9.51, 9.80; H 2.88, 2.85; S 24.44, 24.84. $C_4H_{12}O_4P_2S_4Pb$. Calculated %: C 9.21; H 2.31; S 24.59.

This salt has not been described in the literature. The yield was practically quantitative. In order to identify the phenylmetaphosphate portion, the salt was treated with nitric acid. As a result of this treatment, we obtained p-nitrophenol after hydrolysis.

Under analogous conditions we carried out the reaction of bis(diethoxythiophosphonium)-disulfide with sodium diphenylphosphite. The yield of tetraethyltrithiopyrophosphate was 90%. M.p. 39.5°.

Found %: P 18.41, 18.47. $C_8H_{20}O_4S_3P_2$. Calculated %: P 18.36.

The yield of triphenylthiophosphate was 73%. M.p. 48-49°. Yield of lead salt 92%. M.p. 74° [11].

SUMMARY

We have studied the reaction of triaryl- and diarylphosphites with bis(dialkoxythiophosphonium)-disulfides. We have shown that the chief reaction products of the reaction of triarylphosphites with bis(dialkoxythiophosphonium)-disulfides are tetraalkyltrithiopyrophosphates and triarylthiophosphates. The diarylphosphites with the disulfides, besides this, form salts of dialkyldithiophosphoric acid and metaphosphate. We have shown that the direction of the reaction of triarylphosphites and trialkylphosphites with bis(dialkoxythiophosphonium)-disulfides is related to the mobility of the ester radical.

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*Original Russian pagination. See C. B. translation.

SOME DERIVATIVES OF 5-HALOFURAN CARBOXYLIC ACIDS

Z. N. Nazarova and I. G. Gakh

Rostov-on-Don State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2322-2326, July, 1960
Original article submitted July 8, 1959

The method which we previously worked out [1-3] for preparing 5-halofurfurols X-(C_4H_2O)-A (I, A=CHO; X=Cl, Br, I) has permitted using them as a basis for obtaining not only different 2-vinylated 5-halofurans [2-6],

where A = $CH=C(NO_2)_2$, $CH=C(Cl)(NO_2)$ CH=CHCOOH, CH=CHCOR and others (ketonic condensation), but also,

by exchange of the halogen in the latter, to obtain various 5-substituted furan derivatives (X=I, NO_2, CN, SCN, OR, OAr etc.).

The 5-halofurfurol which we synthesized can easily be transformed by the Cannizzaro reaction into 5-halofuran carboxylic acid. This reaction is of real value for obtaining the 5-chloro-[7] and especially the 5-iodofuran carboxylic acid [2] which are difficult to get by other methods, for the direct halogenation of furan carboxylic acid is of value only in obtaining 5-bromofuran carboxylic acid [8].

The purpose of our work is to explain the mobility of the halogen in our 5-halofuran carboxylic acids and their derivatives

$$X=(C_4H_2O)-C(=O)-B \quad (II,\ X=Br,\ I;\ B=OH, OR, Cl, NH_2, NHAr)$$

and to compare this with the mobility of halogens in other 5-bromo-substituted furans [2,4-6]. For this reason we synthesized the 5-halofuran carboxylic acids (II, B=OCH_3, Cl, NH_2, NHAr; X=Br, I; Ar=C_6H_5, $C_6H_4OCH_3$).

5-Iodofuran carboxylic acid, which could not be obtained by direct iodination (the literature contains no mention of its derivatives) was obtained by the Cannizzaro reaction [2]. By heating 5-iodofuran carboxylic acid with $SOCl_2$ we obtained the acid chloride. When this was treated with a concentrated aqueous solution of ammonia, we easily obtained the amide (II, B=NH_2, X=I), with aromatic amines, the corresponding anilide (II, B=NHAr, X=I). By treatment with methanol we obtained the methyl ester (II, B=OCH_3, X=I) and when the acid chloride was heated with a solution of sodium in methanol, we obtained besides the methyl ester of 5-methoxyfuran carboxylic acid (III) also 5-methoxyfuran carboxylic acid (IV). Both the latter compounds have been described in the literature [10]. When it is boiled with water or dilute alkali, the acid chloride is completely hydrolyzed with formation of 5-iodofuran carboxylic acid. We have shown that the methoxy derivatives (III and IV) can be obtained only by heating the methyl ester of 5-iodofuran carboxylic acid with sodium methylate.

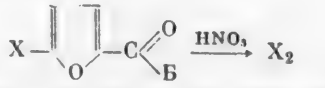
5-Bromofuran carboxylic acid was obtained by us by a somewhat modified method [8] of direct bromination

of the furan carboxylic acid with a yield of 75%, and from it we prepared the acid chloride [9], methyl ester, and undescribed anilide. When the acid chloride of 5-bromofuran carboxylic acid was heated with NaI in anhydrous acetone there occurred only the formation of 5-bromofuran carboxylic acid acid iodide; here bromine did not enter into an exchange reaction. We did not succeed in our attempt to replace bromine by iodine in 5-bromofuran carboxylic acid and its methyl ester by analogy with replacement of bromine by iodine in the methyl ester of 5-bromofurylacrylic acid [4]. Neither does replacement of bromine by iodine occur in the anilide of 5-bromofuran carboxylic acid.

These facts indicate the lower mobility of bromine in derivatives of 5-bromofuran carboxylic acid (acid chloride, anilide, and methyl ester) under nucleophilic attack by alkali iodides as compared to the mobility of bromine in the methyl ester of 5-bromofurylacrylic acid [4]. However, bromine in derivatives of 5-bromo and 5-iodofuran carboxylic acid can be replaced by the methoxy group under the action of a solution of sodium methylate in methanol.

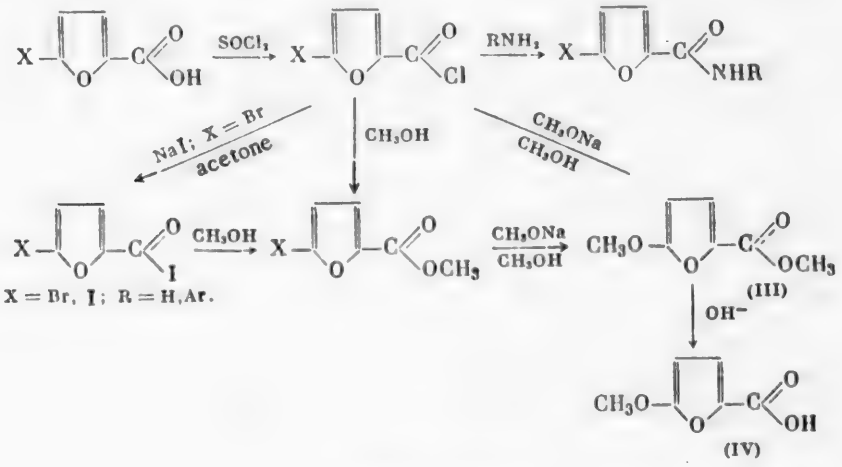
Thus, the success of the exchange reaction of halogen depends not only on the relative mobility of the halogen in the 5-position of the furan ring (I) and the conditions of the reaction, but also to a considerable extent on the activity of the attacking nucleophilic reagent. Attack by the nucleophilic reagent CH_3O^-, which is stronger than I^-, leads to replacement of the halogen in derivatives of 5-halofuran carboxylic acid (II, X=Br, I; B=OCH_3, Cl).

All the derivatives of 5-bromo-and 5-iodofuran carboxylic acid, like the acids themselves, give up iodine quantitatively under the influence of concentrated HNO_3.



X = Br, I; B = OH, Cl, NH_2, NHAr, OCH_3.

The transformations which we have carried out are summarized in the following scheme:



X = Br, I; R = H, Ar.

EXPERIMENTAL

5-Bromofuran carboxylic acid. a) A solution of 3.5 g of 5-bromofurfurol in 20 ml of ether was energetically stirred for several hours with 80 ml of 30% NaOH solution which contained several drops of 30% H_2O_2 [7]. When flakes appeared, the mixture was allowed to stand for a day. Yield 1.52 g (40%). 5-Bromofurfurylic alcohol could be isolated from the ether extract.

b) Eighty g of pyromucic acid* was placed in a three necked flask with a reflux condenser, dropping funnel, and stirrer, 60 ml of glacial acetic acid was added, the mixture was heated gently on the water bath, the stirrer was started, and a solution of 100 ml of bromine in 100 ml of glacial acetic acid was added dropwise with strict attention to the temperature of the mixture. When vapors of bromine appeared in the condenser, heating was

*Pyromucic acid was obtained according to the method in the literature [11].

stopped; if crystals of the acid began to appear on the walls of the flask, heating had to be recommenced. Strong heating could lead to carbonization. Then the mixture was boiled on the water bath until evolution of HBr stopped (about 5 hours), cooled, dissolved in 1.2 liters of boiling water, boiled with charcoal, and filtered. After cooling, the acid crystallized in the form of white needles. Yield 60 g (60%). M. p. 187°. It was possible to isolate from the mother liquors another 15 g of acid. Total yield 75 g (75%).

Anilide of 5-bromofuran carboxylic acid [12]. To 2.09 g of acid chloride of 5-bromofuran carboxylic acid in 5 ml of absolute ether was added a solution of 0.9 g of aniline in 5 ml of absolute ether, dropwise and with cooling. A precipitate of the anilide formed at once. It was dissolved in 25 ml of 80% acetic acid and 25 ml of hot water was added; with gradual cooling, white needles formed. Yield quantitative. M.p. 143-144° (from acetone).

Found %: N 5.58, 5.36. $C_{11}H_8O_2NBr$. Calculated %: N 5.26.

5-Bromofuran carboxylic acid iodide. When 1.05 g of 5-bromofuran carboxylic acid chloride, 1.5 g of anhydrous NaI, and 10 ml of anhydrous acetone were heated on a water bath a precipitate of sodium chloride quickly came down. The mixture was heated for 15 minutes more and then filtered hot. When the acetone was evaporated off under a slight vacuum, a dark residue remained of the very unstable 5-bromofuran carboxylic acid iodide, which decomposed on standing, with evolution of iodine. When it was treated with water, it hydrolyzed with formation of 5-bromofuran carboxylic acid (m.p. 184°), which after treatment with concentrated ammonia gave the amide of 5-bromofuran carboxylic acid (m.p. 143° [13]).

5-Iodofuran carboxylic acid chloride. To a solution of 11.9 g of 5-iodofuran carboxylic acid in 12 ml of anhydrous benzene was added 8 ml of freshly distilled thionyl chloride. The mixture was boiled on the water bath for 3.5 hours, after which the excess $SOCl_2$ and C_6H_6 were distilled off in a vacuum. The residue crystallized completely. Yield 10.8 g (87%). M.p. 68° (from benzene); from acetone, a white crystalline substance which gradually darkened in color when kept. When heated with HNO_3, it evolved iodine quantitatively [2].

Found %: (I+Cl) 62.96, 63.04. $C_5H_2O_2ClI$ Calculated %: (I+Cl) 63.31.

When boiled with water, the acid chloride, more quickly in the presence of alkali, gave 5-iodofuran carboxylic acid with m.p. 197° (from benzene).

Methyl 5-iodofuran carboxylate. To a benzene solution of 5 g of 5-iodofuran carboxylic acid chloride was added a five-fold excess of anhydrous CH_3OH and the mixture was allowed to stand for two days. After distillation of the benzene on the water bath, light brown crystals precipitated; after washing with ligroin, white needles with m.p. 82°. We obtained 3 g (60%); iodine was evolved quantitatively by heating with HNO_3.

Found %: I 50.05, 50.17. $C_6H_5O_3I$. Calculated %: I 50.36.

Easily soluble in benzene, pooly so in ligroin, with darkening of the color.

5-Iodofuran carboxylic acid amide. When a solution of 1.7 g of 5-iodofuran carboxylic acid chloride in 10 ml of anhydrous benzene was treated with concentrated ammonia, there at once appeared a precipitate of white crystals of 5-iodofuran carboxylic acid amide. Yield 1.1 g (90%), m.p. 116° (from benzene). After long standing in the light, it darkened. When boiled with water in the presence of acid, followed by making the solution alkaline, the amide was hydrolyzed with evolution of ammonia; when heated with HNO_3, it evolved iodine quantitatively.

Found %: N 5.56, 5.49; I 52.67, 52.84. $C_5H_4NO_2I$ Calculated %: N 5.90; I 53.55.

5-Iodofuran carboxylic acid anilide. We obtained it as described above, from 0.51 g of acid chloride, 5 ml of absolute ether, and 0.19 g of aniline in 2 ml of absolute ether. Yield quantitative. M.p. 159-159.5° (from alcohol). White needles.

Found %: N 4.62, 4.37. $C_{11}H_8NO_2I$. Calculated %: N 4.47.

5-Iodofuran carboxylic acid p-methoxyanilide. To 0.5 g of 5-iodofuran carboxylic acid chloride in 5 ml of absolute ether we added 0.25 g of p-anisidine. The reaction occurred without heating. Then we added 12 ml of 70% CH_3COOH and 5 ml of hot water; the mixture stood for a day. We obtained 0.47 g (62%) with m.p. 134°.

Found %: N 4.20, 3.93. $C_{11}H_{10}NO_3I$. Calculated %: N 4.24.

5-Methoxyfuran carboxylic acid and its methyl ester. a) To a solution of sodium methylate in methanol from 0.46 g of Na in 30 ml of anhydrous CH_3OH we added in small portions (cooling with water) 2.565 g of 5-iodofuran carboxylic acid chloride. A white precipitate (NaCl + NaI at once appeared. The mixture was heated for one hour on a water bath, the methanol was distilled off in a vacuum, and the residue was treated with 30 ml of ether and 50 ml of water. We isolated from the ether layer 0.77 g (49.4%) of methyl 5-methoxyfuran carboxylate, m.p. 54-55° (from benzene). According to [10], m.p. 51-53°. From the water layer by careful acidification, with cooling and in the presence of ether, we isolated 0.2 g of 5-methoxyfuran carboxylic acid, m.p. 142-143° (according to [10], m.p. 136-141°).

Found equiv. 143. $C_6H_6O_4$. Calculated equiv. 142.

b) A mixture of 2.52 g of methyl 5-iodofuran carboxylate and a solution of sodium methylate (from 0.23 g Na in 20 ml of anhydrous methanol) was heated 1.5 hours on a water bath under reflux. After treatment like the previous one, we obtained 0.78 g (50%) of methyl 5-methoxyfuran carboxylate (m.p. 52-53°) and 0.1 g of 5-methoxyfuran carboxylic acid (m.p. 141-142°).

SUMMARY

1. We have obtained the undescribed 5-halofuran carboxylic acid derivatives: acid chloride, methyl ester, amide, anilide, and p-methoxyanilide of 5-iodofuran carboxylic acid, and also the acid iodide and anilide of 5-bromofuran carboxylic acid.

2. In the derivatives of 5-bromofuran carboxylic acid (anilide, acid chloride, and methyl ester) the bromine is less mobile under nucleophilic attack by alkali iodides than it is in methyl 5-bromofuran carboxylate.

3. We have shown the possibility of replacement of iodine by the methoxy group in the reaction of 5-iodofuran carboxylic acid chloride or its methyl ester with a solution of sodium methylate in methanol.

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*Original Russian pagination. See C. B. translation

**See C. B. translation.

SYNTHESES AND REARRANGEMENTS IN THE THIAZOLINE IMINE SERIES

I. THE CONDENSATIONS OF CHLOROACETONE AND α-CHLOROCYCLOHEXANONE WITH SYMMETRICAL DIARYL- AND ARYLACYLTHIOUREAS

K. M. Murav'eva and M. N. Shchukina

S. Ordzhonikidze All-Union Research Chemicopharmaceutical Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2327-2334, July, 1960
Original article submitted June 9, 1959

It is known that thiourea and its N-substituted derivatives react with α-haloketones with the formation of thiazole derivatives. Intermediate compounds have not been isolated here, since the reaction occurs energetically and it could not be stopped in the first stage. One of us with P. M. Kochergin showed by the example of condensation of α-haloketones and bromoacetaldehyde with substituted 2-mercaptoimidazoles that the formation of imidazo-(2,1-b)-thiazoles occurs through the intermediate stage of S-β-carbonyl compounds with later formation of the hydroxythiazoline ring [1, 2].

In further work we studied the formation of the thiazoline ring in the example of the condensation of chloroacetone with N,N'-diaryl- and N-aryl-N'-acylthioureas, and also of α-chlorocyclohexanone with N-aryl-N'-acylthioureas. The final reaction product with N-aryl-N'-acylthioureas is the corresponding 2-acylimino-4-thiazoline. We confirmed that the course of the reaction depends on the presence in the reaction medium of hydrogen ions. If the hydrogen chloride which is formed is bound by sodium alcoholate or triethylamine, then the reaction stops at the stage of 4-hydroxythiazolidine derivatives.

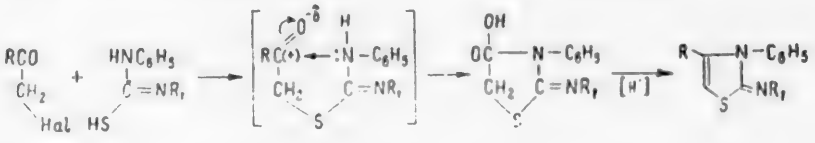
These intermediate compounds are not stable, especially if the initial substances were N,N'-diarylthioureas. For example, in the condensation of chloroacetone with N,N'-diphenylthiourea at room temperature in methylene chloride solution in the presence of triethylamine we could obtain 2-phenylimino-3-phenyl-4-methyl-4-hydroxythiazolidine (Ia), but this substance even when heated below its melting point and even on recrystallization from alcohol lost water and was converted into 2-phenylimino-3-phenyl-4-methyl-4-thiazoline (I) [3]. In the condensation of N,N'-ditolyl- and diphenylthioureas with chloroacetone, the intermediate 4-hydroxythiazolidine compounds could not be isolated.

The intermediate reaction product of chloroacetone and N-phenyl-N'-acylthioureas is simpler. When hydrochloric acid acts on cold 2-acylimino-3-phenyl-4-hydroxythiazolidine, water is split out, leading to the corresponding thiazoline compound. Thus, from chloroacetone and N-phenyl-N'-benzoylthiourea we obtained 2-benzoylimino-3-phenyl-4-methyl-4-hydroxythiazolidine (IVa), and 2-benzoylimino-3-phenyl-4-methyl-4-thiazoline (IV); from chloroacetone and N-phenyl-N'-p-nitrobenzoylthiourea, 2-(p-nitrobenzoylimino)-3-phenyl-4-methyl-4-hydroxythiazolidine (Va) and 2-(p-nitrobenzoylimino)-3-phenyl-4-methyl-4-thiazoline (V); and an analogous pair of substances from chloroacetone and N-phenyl-N'-acetylthiourea (VI, VIa); from α-chlorocyclohexanone and N-phenyl-N'-acetylthiourea was obtained 2-acetylimino-3-phenyl-4-hydroxy-4,5-cyclotetramethylenethiazolidine (VIIa) and 2-acetylimino 3-phenyl-4,5-cyclotetramethylene-4-thiazoline (VII). In the condensation of α-chlorocyclohexanone with N-phenyl-N'-benzoylthiourea in methylene chloride at room temperature was obtained a substance which showed qualitatively the presence of hydroxy groups and which was evidently a mixture of a 4-hydroxythiazolidine compound with 2-benzoylimino-3-phenyl-4,5-cyclotetramethylene-4-thiazoline (VIII), a compound which even on crystallization loses water with formation of (XIII). In the reaction of N-phenyl-N'-

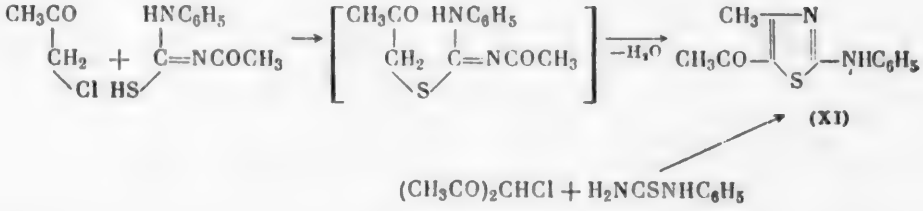
p-nitrobenzoylthiourea with α-chlorocyclohexanone the intermediate compound also cannot be isolated, and we obtained 2-(p nitrobenzoyl)-imino-3-phenyl-4,5-cyclotetramethylene-4-thiazoline (IX). The instability of the 4-hydroxy compounds in these cases can be explained by the nonplanar conformation of the cyclohexane ring [4]. When α-chlorocyclohexanone is heated with N-phenyl-N'-acetylthiourea in alcohol solution splitting of the acetyl group occurs, with formation of 2-imino-3-phenyl-4,5-cyclotetramethylene-4-thiazoline (X) and therefore substance (VII) can be obtained only through the stage of the 4-hydroxythiazolidine compound.

In all cases, the presence of the hydroxy group in the hydroxythiazolidine compounds was shown by the presence of absorption bands in the infrared spectra in the region 3080-3560 cm^{-1}, characteristic for the OH group. Lines characteristic of ketone carbonyl (1740-1760 cm^{-1}) were absent, and the substances did not show reactions typical of the ketone group. The determination, according to Tserevitinov, showed the presence of one active hydrogen, and the 4-hydroxythiazolidine derivative (VIIa) gave two moles of methane which corresponded to the behavior of an alcohol with hydrogen on the tertiary β-carbon atom.

We can conclude from these reaction that the following mechanisms of formation of the thiazoline ring occur. The isoforms of the substituted thioureas react with α-haloketones forming S-β-ketosubstituted isothioureas, which, because of the presence of the reciprocally reactive carbonyl and imino groups are converted with rearrangement of the hydrogen from the amino group to the carbonyl residue in the 4-hydroxythiazolidine derivatives. These compounds lose water giving the corresponding substituted 2-imino-4-thiazolines.



Confirmation of the fact that the first intermediate stage of the reaction is the splitting of a halogen hydride with formation of S-β-keto derivatives of isothiourea comes from the fact that in the condensation of chloroacetone and N-phenyl-N'-acetylthiourea in boiling alcohol in the presence of triethylamine we obtained 2-phenylamino-4-methyl-5-acetylthiazole (XI) whose structure was shown by synthesis from diacetylchloromethane and phenylthiourea. The formation of substance (XI) can be explained by cyclization of the intermediate S-acetonyl-N-phenyl-N'-acetylisothiourea with splitting out of water because of the methylene group and oxygen in the acetyl residue on the nitrogen.



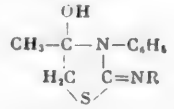
2-Acylimino-4-thiazolines are weak bases. Their hydrochlorides are hydrolyzed even on dilution of the solutions with water. The 2-acylimino-4-thiazolines which we obtained (IV, V, VI) when heated in aqueous alcohol solutions of hydrochloric acid are hydrolyzed with formation of 2-imino-3-phenyl-4-methyl-4-thiazoline (XII) [5]. Substances (VII, VIII, IX) when heated with alcoholic hydrochloric acid are hydrolyzed to (X).

The 2-imino-3-phenyl-4-substituted thiazoline (XII) and (X) are converted by acylation into the starting 2-acylimino derivatives of thiazoline.

EXPERIMENTAL

2-Phenylimino-3-phenyl-4-methyl-4-hydroxythiazolidine (Ia). To a solution of 2.28 g (0.01 mole) of thiocarbanilide in 50 ml of methylene chloride was added 3 ml of triethylamine and 1.85 g (0.02 mole) of chloroacetone. The mixture was shaken for several hours. The yellowed solution was evaporated in a vacuum and the solid residue was washed with water and cold alcohol. We obtained 2.7 g (95.5%) of a white crystalline substance with m.p. 134-136°. After recrystallization from ether m.p. 137-138°. We obtained the hydroxythiazolidine compounds shown in Table 1 by this method. Substance (IVa) was obtained from 5.12 g (0.02 mole) of N-phenyl-

TABLE 1. 4-Hydroxythiazolidines



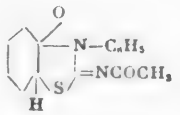
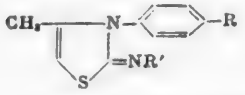
Substance	R	Yield, %	Reaction conditions			M. p.	Empirical formula	Found, %					Calculated, %				
			medium	temperature	duration, hours			C	H	N	S	OH	C	H	N	S	OH
(Ia)	C_6H_5	95.5	CH_2Cl_2	20°	8	137—138°	$C_{16}H_{16}ON_2S$	67.81	5.63	10.15	10.97	5.32	67.7	5.65	9.92	11.25	5.65
(IVa)	C_6H_5CO	85.5	CH_2Cl_2	20	44	158—160	$C_{17}H_{16}O_2N_2S$	65.86	5.37	8.88	9.93	5.75	65.34	5.16	8.97	10.25	5.44
		66.0	C_2H_5OH	70	2.5												
(Va)	p-$NO_2C_6H_4CO$	67.5	C_2H_5OH	70	4.5	160—162	$C_{17}H_{15}O_4N_3S$	57.33	4.28	11.58	9.14	4.46	57.1	4.23	11.76	8.97	4.06
(VIa)	CH_3CO	42.0	CH_2Cl_2	20	119	132.5—133.5	$C_{12}H_{14}O_2N_2S$	57.51	5.71	11.30	12.99	8.34	57.58	5.64	11.19	12.81	6.8
		38.0	C_6H_6	80	0.5												
(VIIa)		34.3	C_2H_5OH	70	4	158—159	$C_{15}H_{18}O_2N_2S$	62.16	6.37	9.52	10.97	11.45	62.05	6.25	9.65	11.04	5.86

TABLE 2. Substituted 2-Imino-4-thiazolines



Substance	R	R′	Yield, %	Reaction conditions: medium	Reaction conditions: temperature	Reaction conditions: duration, hours	M. p.	Empirical formula	Found, %: C	Found, %: H	Found, %: N	Found, %: S	Calculated, %: C	Calculated, %: H	Calculated, %: N	Calculated, %: S
(I)	H	C_6H_5	83	C_2H_5OH	70°	1	138—139°									
(II)	CH_3	p-$CH_3C_6H_4$	61.7	C_2H_5OH	70	3	111—113	$C_{18}H_{18}N_2S$	73.33	6.00	9.37	11.04	73.8	6.31	9.55	10.89
			78.8	CH_2Cl_2 [in presence of $(C_2H_5)_3N$]	20	97	111—112									
(III)	OC_2H_5	p-$C_2H_5OC_6H_4$	78.0	C_2H_5OH	70	2	162—163	$C_{20}H_{22}O_2N_2S$	67.8	6.13	7.82	9.01	68.00	6.28	7.93	9.08
			71.0	CH_2Cl_2 [in presence of $(C_2H_5)_3N$]	20	180										
(IV)	H	C_6H_5CO	71.0	CH_2Cl_2	20	240	156—158	$C_{17}H_{14}ON_2S$	69.24	4.85	9.48	10.70	69.37	4.8	9.5	10.89
			30.2	n-Butyl alcohol	117	2										
(V)	H	p $NO_2C_6H_4CO$	33.0	n-Butyl alcohol	117	2	184—185	$C_{17}H_{13}O_3N_3S$	60.14	3.84	12.38	9.67	60.16	3.86	12.38	9.45

N-benzoylthiourea and 3.67 g (0.027 mole) of chloroacetone in the presence of 12 ml of triethylamine, and substance (VIa) from 7.76 g (0.04 mole) of N-phenyl-N'-acetylthiourea and 7.38 g (0.08 mole) of chloroacetone in the presence of 12 ml of triethylamine. After reaction, substances (IVa) and (VIa) partly precipitated from solution. They were filtered and washed with water and cold alcohol. Evaporation of the methylene chloride mother liquor gave a further amount of (IVa) and (VIa). For analysis substance (IVa) was recrystallized from alcohol as thick, glittering hexagonal plates; substance (VIa) was recrystallized from benzene as colorless needles. The wash water from (VIa) after being made alkaline gave 5% 2-phenylamino-4-methyl-5-acetylthiazole (XI), m.p. 152-153°. Colorless needles (from alcohol) in the form of clumps, soluble in most organic solvents.

Found %: C 62.06; H 5.15; N 12.13; S 13.61. $C_{17}H_{14}N_2OS$. Calculated %: C 62.04; H 5.06; N 12.06; S 13.80.

Substance (VIa) was also obtained by heating the components in benzene, and (IVa) by boiling the components in anhydrous alcohol. Under the same conditions of heating in alcohol we obtained (Va) from 6.03 g (0.02 mole) of N-phenyl-N'-(p-nitrobenzoyl)-thiourea and 1.8 ml (0.023 mole) of chloroacetone in the presence of 3 ml of triethylamine, and (VIIa) from 7.76 g (0.04 mole) of N-phenyl-N'-acetylthiourea and 9.2 ml (0.08 mole) of α-chlorocyclohexanone with 14 ml of triethylamine. For analysis the substances were recrystallized from alcohol: (Va) as yellow prisms, and (VIIa) as a colorless crystalline substance.

2-Phenylimino-3-phenyl-4-methyl-4-thiazoline (I). A mixture of 0.23 g (0.001 mole) of thiocarbanilide and 0.19 g (0.002 mole) of chloroacetone in 20 ml of anhydrous alcohol was boiled for one hour and evaporated dry. The oily residue was treated with water and ether. From the dried ether solution, after distillation of the ether we obtained 0.11 g of substance (I), and from the water solution, made alkaline with ammonia, another 0.11 g (total yield 83%). After recrystallization from alcohol, m.p. 138-139° [3]. Substance (I) is much more soluble in ether than is (Ia). By this method we obtained compounds (II) from 2.56 g (0.01 mole) of 4,4'-dimethylthiocarbanilide and 1.82 g of chloroacetone (0.02 mole); (III) from 3.16 g (0.01 mole) of 4,4'-diethoxythiocarbanilide and 1.85 g (0.02 mole) of chloroacetone (see Table 2).

Compound (III) is less soluble in ether than are (I) and (II) and so after evaporation the residue was treated with water, filtered, and washed to absence of reaction for halogen. Making the aqueous mother liquor alkaline with ammonia gave a further amount of (III).

Substances (II) and (III) were also obtained by shaking the components in the presence of 3.5 ml of triethylamine in methylene chloride solution. Samples mixed with forms obtained in alcohol solution gave no depression. Substance (II), colorless needles (from alcohol); (III), long colorless needles (from alcohol).

Substance (VIII) was obtained by boiling 10.24 g (0.04 mole) of N-phenyl-N'-benzoylthiourea and 18.5 g (0.14 mole) of α-chlorocyclohexanone in 20 ml of alcohol. Yield 0.85 g, m.p. 197-200°. After recrystallization from alcohol, colorless needles with m.p. 204-205°.

Found %: C 72.12; H 5.38; N 8.30; S 9.40. $C_{20}H_{18}ON_2S$. Calculated %: C 71.85; H 5.42; N 8.38; S 9.59.

From the aqueous mother liquors of the reaction we isolated with ammonia 2.55 g of 2-imino-3-phenyl-4,5-cyclotetramethylene-4-thiazoline (X).

Compound (VIII) was also obtained by shaking a solution of 5.12 g (0.02 mole) of N-phenyl-N'-benzoylthiourea in 40 ml of methylene chloride with 6 ml of triethylamine and 5.2 g (0.039 mole) of α-chlorocyclohexanone. The precipitate of triethylamine hydrochloride was filtered off and the mother liquor was evaporated dry. The caramel-like residue was ground with a small amount of alcohol, the resulting precipitate was filtered and washed repeatedly with cold alcohol. We obtained 3.58 g of a colorless, crystalline substance which was dissolved in concentrated hydrochloric acid and precipitated by ammonia. After recrystallization from alcohol we obtained 2.88 g (43%) of (VIII), m.p. 204-205°.

Substance (VIII) was also obtained after seven hours boiling of the components in anhydrous alcohol, yield 34%. A test of this with (VIII) obtained without addition of triethylamine gave no depression.

2-Acetylimino-3-phenyl-4-methyl-4-thiazoline (VI) was obtained by boiling for 2.5 hours of 7.2 g (0.037 mole) N-phenyl-N'-acetylthiourea and 7 ml (0.0878 mole) of chloroacetone in 60 ml of anhydrous alcohol.

After evaporation the residue was washed with water. On the filter remained 1.77 g of unchanged substance. Addition of ammonia precipitated from the mother liquor 4.84 g of substance. After recrystallization from alcohol we obtained 3.2 g (49.5%) of colorless prisms, compacted in clumps. Substance (VI) was also obtained by acetyla-

tion of substance (XII) by acetic anhydride with a yield of 92%, m.p. 182-183° (according to the literature m.p. 182° [5], 181-182° [6]); all the forms gave mixed melting points without depression.

2-Benzoylimino-3-phenyl-4-methyl-4-thiazoline (IV). a) A solution of 5.12 g (0.02 mole) of N-phenyl-N'-benzoylthiourea in 50 ml of methylene chloride and 2.43 g (0.026 mole) of chloroacetone was shaken for several days and evaporated dry. The residue was washed with water, alcohol, and ether. We obtained 5 g of substance with m.p. 115-138° which was treated with hydrochloric acid. On this, 1.5 g of unchanged N-phenyl-N'-benzoylthiourea did not dissolve. From the hydrochloric acid solution after dilution with water and treatment with ammonia was obtained 3.5 g of substance (IV). After recrystallization from alcohol, colorless rhombic plates with m.p. 156-158°, 2.95 g (71%).

b) To a suspension of 5.12 g (0.02 mole) of N-phenyl-N'-benzoylthiourea in 20 ml of butyl alcohol was added 1.85 g (0.02 mole) of chloroacetone and the mixture was boiled with stirring for two hours. After cooling, a white precipitate separated. It was washed with alcohol and ether and treated with hydrochloric acid in experiment "a". We isolated 0.15 g of N-phenyl-N'-benzoylthiourea and 2.08 g of a substance which after recrystallization from alcohol gave 1.72 g (30.2%) of (IV) with m.p. 156-158°. From the aqueous mother liquor we isolated with ammonia 1.3 g (35.3%) of 2-imino-3-phenyl-4-methyl-4-thiazoline (XII) with m.p. 84-86°, by benzoylation of which we obtained (IV) also.

By process "b" from 6.03 g of N-phenyl-N'-(p-nitrobenzoyl)-thiourea and 1.7 g of chloroacetone we obtained substance (V), and from 6.03 g of N-phenyl-N'-(p-nitrobenzoyl)-thiourea and 3 ml of α-chlorocyclohexanone, substance (IX). The yellow precipitate was washed with alcohol. We obtained 1.46 g (19%). After recrystallization from alcohol, yellow prisms with m.p. 167.5-169°.

Found %: C 63.36; H 4.62; N 11.00; S 8.55. $C_{20}H_{17}O_3N_3S$. Calculated %: C 63.31; H 4.51; N 11.08; S 8.45.

By making the mother liquor alkaline we obtained some quantity of substance (X).

Substance (IX) was also obtained by boiling a suspension of 6.03 g of N-phenyl-N'-(p-nitrobenzoyl)-thiourea in 20 ml of anhydrous alcohol and 5.8 ml of triethylamine, to which was added with stirring 4.65 ml of α-chlorocyclohexanone in 5 ml of alcohol. The mixture was boiled for five min and evaporated dry in a vacuum. Water and ether were added to the residue. The precipitate which formed between the layers was separated. The yield of substance (IX) was 1.88 g (25%). After recrystallization from alcohol, yellow prisms with m.p. 167.5-169°. A mixed melting point with (IX) prepared above gave no depression.

Compounds (I, IV, V, VI, VII) were also obtained by solution of (Ia, IVa, Va, VIa, VIIa) in hydrochloric acid with subsequent dilution with water and addition of ammonia.

2-Phenylamino-4-methyl-5-acetylthiazole (XI). a) To a boiling solution of 15.56 g of N-phenyl-N'-acetylthiourea and 22.4 ml of triethylamine in 80 ml of anhydrous alcohol was added with stirring 12.8 ml of chloroacetone, and boiling was continued for three hours. The solution was evaporated dry and the residue was washed with water and cold alcohol. After recrystallization from 50% alcohol we obtained 8.67 g (46.6%) of substance (XI) with m.p. 152-153°. Colorless needles from alcohol, crystallizing in clumps, soluble in most organic solvents.

b) A mixture of 1.52 g of phenylthiourea and 1.7 g of diacetylchloromethane and 50 ml of anhydrous alcohol was boiled with stirring for two hours. The precipitate was filtered off and washed repeatedly with water and alcohol. We obtained 1.65 g of white, crystalline substance (XI), m.p. 149.5-151°. Further separation by making the mother liquor alkaline, 0.3 g. Total yield 84.5%. A sample mixed with (XI) obtained above gave no depression of the melting point.

Action of aqueous alcoholic hydrochloric acid on 2-acylimino derivatives of 4-thiazolines. a) When substances (IV, V, VI) were boiled with hydrochloric acid in aqueous-alcoholic solution, after evaporation and making the solution alkaline with ammonia, we isolated a quantitative yield of 2-imino-3-phenyl-4-methyl-4-thiazoline (XII), easily soluble in most organic solvents, and poorly in ligroin. After its purification through the hydrochloride with later recrystallization of the base from aqueous alcohol and then ligroin, m.p. 85-86° (80° [5]). When acetic anhydride acted on substance (XII) we obtained an acetyl derivative with m.p. 182-183° which gave no melting point depression with substance (VI). On benzoylation by the Schotten-Baumann reaction we obtained the 2-benzoylimino derivative which in a mixture with substance (IV) gave no melting point depression.

b) On boiling substances (VII, VIII, IX) in aqueous alcoholic hydrochloric acid we obtained quantitative yields of 2-imino-3-phenyl-4,5-cyclotetramethylene-4-thiazoline (X). After recrystallization from alcohol, colorless rectilinear prisms, m.p. 117-118°.

Found %: C 67.88; H 6.23; N 12.06. $C_{13}H_{14}N_2S$. Calculated %: C 67.76; H 6.13; N 12.17.

On acetylation of substance (X) by acetic anhydride we obtained the acetyl derivative with m.p. 144.5-145.5° which gave no melting point depression with (VII).

N-Phenyl N'-(p-nitrobenzoyl)-thiourea was obtained by heating p-nitrobenzoylthiocyanate [7] and aniline in benzene solution. Yellow needles (from alcohol), with m.p. 174-176°.

Found %: N 13.75. $C_{14}H_{11}O_3N_3S$. Calculated %: N 13.95.

SUMMARY

1. We have shown that the condensation of α-haloketones with sym-diaryl- and arylacylthioureas proceeds through the intermediate stage of formation of 4-hydroxythiazolidine compounds, which were isolated by carrying out the reaction in the presence of triethylamine.

2. Under the action of hydrochloric acid the 4-hydroxythiazolidine compounds split out water and form the corresponding derivatives of 4-thiazoline.

3. Saponification by aqueous alcoholic hydrochloric acid of 2-acylamino-3-phenyl-4-substituted-4-thiazolines leads to the corresponding 2-imino derivatives.

4. In the condensation of chloroacetone and phenylacetylthiourea in alcoholic solution in the presence of triethylamine there is formed 2-phenylamino-4-methyl-5-acetylthiazole as a result of splitting out water because of the methylene group and the acetyl of the intermediate S-acetonyl-N-phenyl-N'-acetylisothiourea.

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SYNTHESES AND REARRANGEMENTS IN THE THIAZOLINE IMINE SERIES

II. THE CONDENSATION OF ω-BROMOACETOPHENONE WITH N-PHENYL-N'-ACYLTHIOUREAS

K. M. Murav'eva and M. N. Shchukina

S. Ordzhonikidze All-Union Research Chemicopharaceutical Institute
Translated from Zhurnal Obshchei Khimii, Vol 30, No. 7, pp. 2334-2340,
July, 1960
Original article submitted June 9, 1959

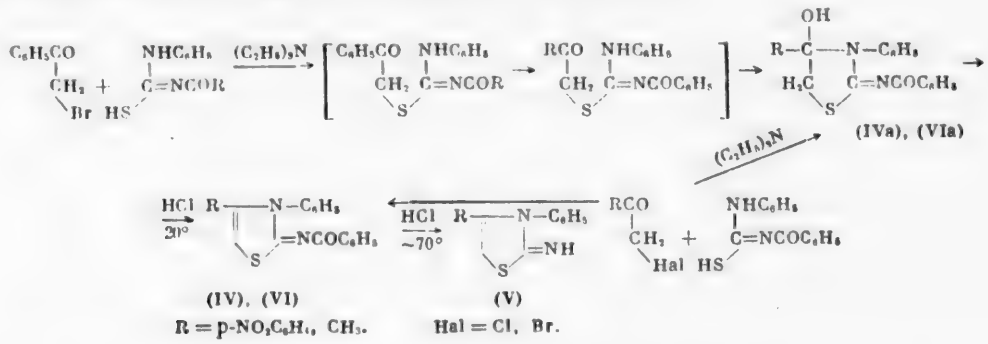
In the previous communication [1] we described the mechanism of formation of 2-acylimino-3-phenyl-4-thiazolines from chloroacetone, α-chlorocyclohexanone, and sym-phenylacylthioureas. In the present paper we report a study of the condensation of aromatic α-haloketones with the same substituted thioureas.

When ω-bromoacetophenone is heated with sym-phenylacylthioureas we have obtained 2-benzoyl-(I), 2-p nitrobenzoyl-(II), and 2-acetylimino-3,4-diphenyl-4-thiazoline (III). The latter compound was identified with the one described in the literature obtained by acetylation of 2-imino-3,4-diphenyl-4-thiazoline [2]. Acyliminothiazoline (I), (II), and (III) heated in aqueous alcoholic hydrochloric acid were saponified into 2-imino-3,4-diphenyl-4-thiazoline, obtained by Beyer from ω-thiocyanatoacetophenone and aniline hydrochloride [2].

When the reaction of condensation of ω-bromoacetophenone with sym-phenylacylthioureas was carried out in the presence of triethylamine, we isolated 4-hydroxythiazolidine derivatives. In all cases the presence of the hydroxy group in these thiazolidine compounds was shown by the presence in the infrared spectra of absorption bands characteristic for the OH group in the region 3230-3360 cm^{-1}, and the absence of bands due to ketone carbonyl (1740-1760 cm^{-1}). The substances obtained also did not show chemical reaction characteristic of the ketone group. Although, in the condensation of N-phenyl-N'-benzoylthiourea with ω-bromoacetophenone in the presence of triethylamine we isolated the intermediate compound 2-benzoylimino-3,4-diphenyl-4-hydroxythiazolidine (Ia) which under the influence of hydrochloric acid is converted into compound (I) with loss of water, yet in the condensation of bromoacetophenone with N-phenyl-N'-p-nitrobenzoylthiourea in the presence of triethylamine the reaction is more complex. Both by heating in anhydrous alcohol or benzene or in methylene chloride at room temperature we obtained 4-hydroxythiazolidine compounds which showed no intermediate substances in the formation of compound (II). This hydroxy compound was identical with 2-benzoylimino-3-phenyl-4-hydroxy-4-p-nitrophenylthiazolidine (IVa) obtained under the same conditions by the condensation of ω-bromo-p-nitroacetophenone with N-phenyl-N'-benzoylthiourea. Compound (IVa) in the reaction with hydrochloric acid at room temperature loses a molecule of water, giving 2-benzoylimino-3-phenyl-4-p-nitrophenyl-4-thiazoline (IV) which we also obtained by condensation of ω-bromo-p-nitroacetophenone with N-phenyl-N'-benzoylthiourea without binding the hydrogen bromide by a base. When compound (IV) was heated with aqueous alcoholic hydrochloric acid it was saponified with formation of 2-imino-3-phenyl-4-p-nitrophenyl-4-thiazoline (V). The latter was converted by heating with acetic anhydride into 2-acetylimino-3-phenyl-4-p-nitrophenyl-4-thiazoline.

An analogous complex course of the reaction also occurs in the condensation of ω-bromoacetophenone with N-phenyl-N'-acetylthiourea. In the presence of triethylamine there is formed a 4-hydroxythiazolidine derivative identical with that obtained by us under the same conditions from chloroacetone and N-phenyl-N'-benzoylthiourea: 2-benzoylimino-3-phenyl-4-methyl-4-hydroxythiazolidine (VIa) which under the influence of hydrochloric acid gives a 2-benzoylimino-3-phenyl-4-methyl-4-thiazoline (VI), identical with the compound which we described

in the previous paper [1]. This conversion can be explained as follows. ω-Bromoacetophenone reacts with the isoform of substituted thioureas, giving the S-β-ketoderivative of isothiourea.

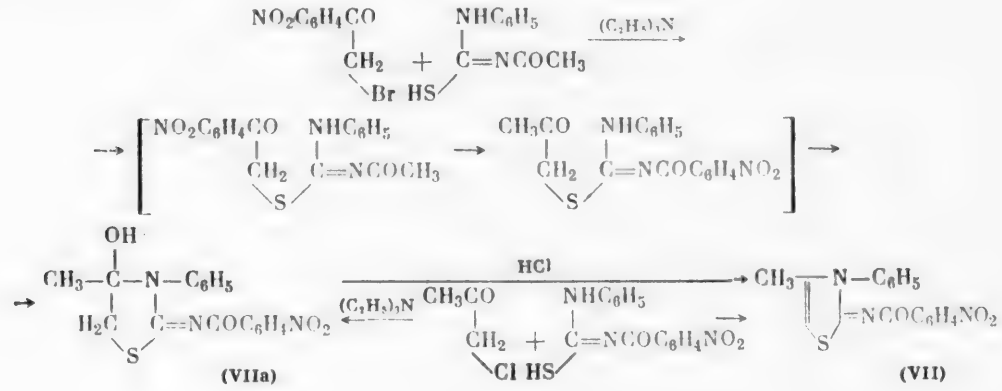


(IV), (VI)
R = p-NO$_2$C$_6$H$_4$, CH$_3$.

(V)
Hal = Cl, Br.

In the latter there evidently occurs a rearrangement of the acyl residue and the benzoyl goes from the methylene group to the nitrogen while the acyl goes from this nitrogen atom to the methylene group. After this there is reaction of the carbonyl and imino groups with formation of 4-hydroxythiazolidine compounds.

To confirm this suggestion we carried out condensation of the components which contained three different substituting groups, ω-bromo-p-nitroacetophenone and N-phenyl-N'-acetylthiourea in the presence of triethyl amine in methylene chloride at room temperature. Here exchange of groups occurred and we obtained 2-p nitrobenzoylimino-3-phenyl-4-methyl-4 hydroxythiazolidine (VIIa) identical with that obtained under the same conditions from chloroacetone and N-phenyl-N'-p-nitrobenzoylthiourea. By solution of compound (VIIa) in concentrated hydrochloric acid it was converted into 2-p-nitrobenzoylimino-3-phenyl-4-methyl-4-thiazoline (VII), identical with that which we described in the previous paper [1].



(VIIa)

(VII)

EXPERIMENTAL

2-Benzoylimino-3,4-diphenyl-4-thiazoline (I). To a suspension of 10.24 g of N-phenyl-N'-benzoylthiourea in 70 ml of anhydrous alcohol was added 8.8 g of ω-bromoacetophenone in 50 ml of alcohol. The mixture was boiled with stirring for five hours. On cooling, 10.48 g of compound (I) separated. Another 1.32 g (83.3%) was obtained from the mother liquors. After recrystallization from alcohol, m.p. 203-204°, colorless needles, soluble in most organic solvents, insoluble in water.

Found %: C 74.10; H 4.55; N 7.77; S 9.10. $C_{22}H_{16}ON_2S$. Calculated %: C 74.13; H 4.52; N 7.86; S 9.00.

The mother liquors after separation of compound (I) were evaporated dry, the residue was extracted with water, and the solution was made alkaline with ammonia. A colorless crystalline substance in the form of needles separated. After washing with water and drying we obtained 0.94 g of 2-imino-3,4-diphenyl-4 thiazoline which was twice recrystallized from aqueous alcohol, m.p. 104-106° (according to the literature, m.p. 111° [2]).

Found %: C 71.56; H 4.5; N 11.09; S 12.84. $C_{15}H_{12}N_2S$. Calculated %: C 71.4; H 4.79; N 11.1; S 12.71.

The picrate had the form of yellow needles from alcohol, m.p. 197–198°, soluble in most organic solvents, insoluble in water.

Found %: N 14.5. $C_{15}H_{12}N_2S \cdot C_6H_3O_7N_3$. Calculated %: N 14.5.

Compound (I) was also obtained by benzoylation of 2-imino-3,4-diphenyl-4-thiazoline and by the action of concentrated hydrochloric acid on compound (Ia) with later isolation of the base by alkali.

2-(p-Nitrobenzoyl)-imino-3,4-diphenyl-4-thiazoline (II). A suspension of 6.03 g of N-phenyl-N'-(p-nitrobenzoyl)-thiourea and 4.5 g of ω-bromoacetophenone in 100 ml of anhydrous alcohol was heated to boiling and stirred. After 15 minutes everything dissolved and then a yellow precipitate formed. After 30 minutes heating was stopped and on cooling the precipitate was filtered and washed with cold alcohol. After two recrystallizations from acetone we obtained 6.65 g (83%) of yellow needles, m.p. 204-205°, poorly soluble in alcohol, insoluble in water.

Found %: C 65.77; H 3.63; N 10.4; S 8.01. $C_{22}H_{15}O_3N_3S$. Calculated %: C 65.82; H 3.76; N 10.47; S 7.99.

2-Acetylimino-3,4-diphenyl-4-thiazoline (III). To a boiling suspension of 3.89 g of N-phenyl-N'-acetylthiourea in 20 ml of anhydrous alcohol was added 4 g of ω-bromoacetophenone in 30 ml of alcohol. The resulting solution was boiled for 10 minutes. On cooling a precipitate came down and was filtered and washed with alcohol and water. We obtained 2.37 g. A further 1.5 g of the substance was obtained from the water and alcohol mother liquors. To remove the starting phenylacetylthiourea, we dissolved the substance in hydrochloric acid, filtered off the small residue, and precipitated with ammonia. We obtained 3.7 g of compound (III) (63%). Colorless prisms from alcohol, m.p. 209.5-210.5° (according to the literature, m.p. 210° [2]).

Action of hydrochloric acid on 2-acylimino derivatives of 4-thiazoline. When compounds (I), (II) and (III) were boiled in aqueous alcoholic hydrochloric acid, after evaporation and addition of ammonia to the solution, we isolated 2-imino-3,4-diphenyl-4-thiazoline, soluble in most organic solvents. After two recrystallizations from aqueous alcohol, m.p. 104–106° (according to the literature, m.p. 111° [2]).

2-Benzoylimino-3,4-diphenyl-4-hydroxythiazolidine (Ia). To a boiling suspension of 5.12 g of N-phenyl-N'-benzoylthiourea in 30 ml of anhydrous alcohol (or dry benzene) and 5.8 ml of triethylamine was added with stirring 7.96 g of ω-bromoacetophenone in 70 ml of anhydrous alcohol during 5 minutes, after which the reaction mass was boiled for 15 minutes more. After cooling, the precipitate was filtered off and washed with water and cold alcohol. The yield of compound (Ia) was 6.71 g (90.3%). Colorless needles from alcohol with m.p. 155.5-156.5°, soluble in methylene chloride, benzene, and ethyl acetate, less so in ether, insoluble in water.

Found %: C 70.30; H 4.67; N 7.74; S 8.53; OH 3.58. $C_{22}H_{18}O_2N_2S$. Calculated %: C 70.55; H 4.84; N 7.48; S 8.56; OH 4.54.

2-Benzoylimino-3-phenyl-4-(p-nitrophenyl)-4-hydroxythiazolidine (IVa). a) From ω-bromo-p-nitroacetophenone and N-phenyl-N' benzoylthiourea. To a solution of 5.12 g of N-phenyl-N'-benzoylthiourea and 3.4 ml of triethylamine in 50 ml of methylene chloride was added a solution of 5 g of ω-bromo-p-nitroacetophenone in 25 ml of methylene chloride. The darkening reaction mass was shaken at room temperature for 4.5 hours. The precipitate was filtered off and washed several times with methylene chloride to remove tarry residues, then with water to remove triethylamine hydrochloride. We obtained 5.36 g of compound (IVa) and from the mother liquors 1.4 g. Yield 80.8%. Fine colorless needles (from benzene), m.p. 158-160°, soluble in dioxane, ethyl acetate, less so in benzene, poorly in alcohols, ether, insoluble in ligroin and water.

Found %: C 63.24; H 4.25; N 10.18; S 7.86; OH 4.46. $C_{22}H_{17}O_4N_3S$. Calculated %: C 62.99; H 4.09; N 10.02; S 7.64; OH 4.06.

b) From ω-bromoacetophenone and N-phenyl-N'-p-nitrobenzoylthiourea. To a boiling suspension of 6.03 g of N phenyl-N'-p-nitrobenzoylthiourea in 30 ml of anhydrous alcohol and 3 ml of triethylamine was added with stirring 4 g of ω-bromoacetophenone in 30 ml of anhydrous alcohol, after which the reaction mixture was boiled for 5 minutes more. After cooling, the precipitate was filtered off and washed with alcohol and water. We obtained 6 g of a colorless, finely crystalline substance and 2.25 g was isolated from the mother liquor. After recrystallization from a mixture of alcohol and acetone and then from benzene, we obtained compound (IVa) with m.p. 159-160°, giving no melting point depression with the sample obtained in the previous experiment. The same substance (IVa) was obtained by carrying out the reaction in methylene chloride solution at room temperature for 50 hours. Compound (IVa) was also obtained by carrying out the condensation in benzene. The reaction was accompanied by evolution of heat.

2-Benzoylimino-3-phenyl-4-p-nitrophenyl-4-thiazoline (IV). A suspension of 3.13 g of 2-phenyl-5-benzoylthiourea and 5 g of ω-bromo-p-nitroacetophenone in 100 ml of anhydrous alcohol was boiled for one hour. With heating occurred solution and then precipitation of a yellow precipitate. After cooling, the precipitate was filtered and washed with alcohol. We obtained 6.35 g of a yellow crystalline substance. We further isolated 0.98 g from the mother liquor. Total yield 80%. Yellow prisms (from acetic acid), m.p. 282-283° (6.24 g, 74.5%), soluble in methylene chloride, acetone, benzene, insoluble in water.

Found %: C 65.98; H 3.74; N 10.56; S 8.18. $C_{22}H_{15}O_3N_3S$. Calculated %: C 65.8; H 3.76; N 10.47; S 7.99.

Compound (IV) was also obtained by the action of concentrated hydrochloric acid on substance (IVa). The resulting compound gave no depression of melting point.

Saponification of 2-benzoylimino-3-phenyl-4-p-nitrophenyl-4-thiazoline (IV). When compound (IV) was boiled with aqueous alcoholic hydrochloric acid for several hours it formed 2-imino-3-phenyl-4-p-nitrophenyl-4-thiazoline (V). The substance was isolated with ammonia, recrystallized from methanol, and then from ethanol: triangular orange plates with m.p. 156-158° (decomposition).

Found %: C 60.90; H 4.01; N 14.09; S 10.62. $C_{15}H_{11}O_2N_3S$. Calculated %: C 60.85; H 3.72; N 14.12; S 10.78.

2-Imino-3-phenyl-4-p-nitrophenyl-4-thiazoline hydrochloride consists of pale yellow prisms from methyl alcohol, m.p. 270-280° (decomposition).

Found %: Cl 10.6. $C_{15}H_{11}O_2N_3S \cdot HCl$. Calculated %: Cl 10.62.

2-Imino-3-phenyl-4-p-nitrophenyl-4-thiazoline picrate consists of yellow prisms from alcohol, m.p. 219-221° (decomposition), soluble in most organic solvents, insoluble in water.

Found %: N 15.98. $C_{15}H_{11}O_2N_3S \cdot C_6H_3O_7N_3$. Calculated %: N 15.9.

Acetylation of 2-imino-3-phenyl-4-p-nitrophenyl-4-thiazoline (V). A solution of 0.11 g of compound (V) in 1.8 ml of acetic anhydride was heated on a boiling water bath for 4 hours. After cooling, the yellow precipitate was filtered and washed with ether. We obtained 0.06 g of substance. A further 0.06 g was isolated from the mother liquors. After two recrystallizations from alcohol, successively methyl and ethyl, we obtained glittering yellow prisms of 2-acetylimino-3-phenyl-4-p-nitrophenyl-4-thiazoline, m.p. 231-232°.

Found %: C 60.33; H 3.80; N 12.58; S 9.2%. $C_{17}H_{13}O_3N_3S$. Calculated %: C 60.35; H 3.86; N 12.38; S 9.48.

2-Benzoylimino-3-phenyl-4-methyl-4-hydroxythiazolidine (VIa). (From ω-bromoacetophenone and N-phenyl-N'-acetylthiourea). To a boiling suspension of 3.59 g of N-phenyl-N'-acetylthiourea in 20 ml of anhydrous alcohol and 5.9 ml of triethylamine was added a solution of 7.96 g of ω-bromoacetophenone in 50 ml of alcohol with stirring during 5 minutes, after which the solution was boiled for 15 minutes more. After cooling, the precipitate was filtered and washed with alcohol and water. We obtained 5.77 g of white, crystalline substance (VIa). After two recrystallizations from alcohol we obtained 4.32 g (70%) of colorless, thick, hexagonal plates, m.p. 158-160°. A mixed melting point with the substance which we obtained by condensation of chloroacetone with N-phenyl-N'-benzoylthiourea [1] gave no depression of the melting point. One g of unpurified substance (VIa) was treated with concentrated hydrochloric acid. The resulting solution was diluted with water and the base was isolated with ammonia. After recrystallization from alcohol we obtained 0.96 g of white crystalline substance as colorless rhombic plates, m.p. 155-157°. A mixed melting point with 2-benzoylimino-3-phenyl-4-methyl-4-thiazoline (156-158° [1]) obtained from chloroacetone and N-phenyl-N'-benzoylthiourea showed no depression.

2-p-(Nitrobenzoylimino)-3-phenyl-4-methyl-4-hydroxythiazolidine (VIIa). (From ω-bromo-p-nitroacetophenone and N-phenyl-N'-acetylthiourea). To a solution of 3.88 g of N-phenyl-N'-acetylthiourea in 110 ml of methylene chloride and 3.2 ml of triethylamine was added 5 g of ω-bromo-p-nitroacetophenone in 50 ml of methylene chloride. The reaction mixture gradually darkened. After shaking for five hours, the solution was evaporated in a vacuum at room temperature. The dark residue was ground with water, filtered, and washed well with water to remove triethylamine hydrochloride, with alcohol, and then with methylene chloride to remove tarry substances. We obtained 4.25 g of yellow substance. After two recrystallizations from alcohol we obtained 2.9 g (about 41%) of substance (VIIa) in the form of yellow prisms, m.p. 160-162°. A mixed sample with 2-p-nitrobenzoylimino-3-phenyl-4-methyl-4-hydroxythiazolidine [1] obtained by condensation of chloroacetone with N-phenyl-N'-p-nitrobenzoylthiourea in the presence of triethylamine showed no melting point depression. Under

the action of concentrated hydrochloric acid (VIIa) at room temperature lost water with formation of 2-p-nitrobenzoylimino-3-phenyl-4-methyl-4-thiazoline (VII). A mixed sample with the form obtained by condensation of chloroacetone with N-phenyl-N'-p nitrobenzoylthiourea [1] gave no melting point depression.

SUMMARY

1. It was shown by the example of the condensation of ω-bromoacetophenone and its p-nitroderivative with N-phenyl-N'-acylthioureas that here the formation of 2-acylimino-3-phenyl-4-substituted 4-thiazolines occurs through the intermediate stage of the corresponding 4-hydroxythiazolidine compound.

2. It was demonstrated that in a number of cases this condensation is accompanied by a rearrangement of the acyl residues in the intermediate S-β-keto derivatives of isothioureas.

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*Original Russian pagination. See C. B. translation.

SYNTHESES AND REARRANGEMENTS IN THE THIAZOLINE IMINE SERIES

III. THE REARRANGEMENT OF 2-IMINO-3-PHENYL-4-THIAZOLINES INTO 2-PHENYLAMINOTHIAZOLES

K. M. Murav'eva and M. N. Shchukina

S. Ordzhonikidze All-Union Research Chemicopharmaceutical Institute

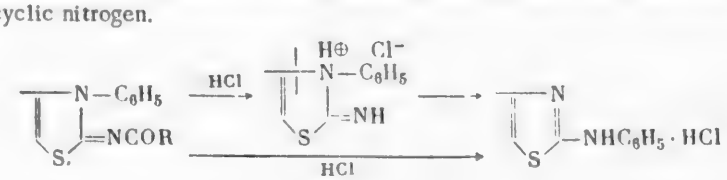
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2340-2343, July, 1960
Original article submitted June 10, 1959

In the previous communications [1,2] we have described the preparation of 2-imino-3-phenyl-4-methyl-4-thiazoline (I), 2-imino-3,4-diphenyl-4-thiazoline (II), 2-imino-3-phenyl-4-p-nitrophenyl-4-thiazoline (III), and 2-imino-3-phenyl-4,5-cyclotetramethylene-4-thiazole (IV) by short heating in aqueous alcoholic hydrochloric acid of the corresponding 2-acylimino compounds.

In carrying out the hydrolysis under more severe conditions, namely, by boiling the acylimine with hydrochloric acid, we have showed that along with the formation of the imino compound there is also obtained a derivative of 2-phenylaminothiazole. The rearrangement of the imines (I, II, III, and IV) into the corresponding 2-phenylaminothiazoles also occurs in direct boiling of the imino compounds with hydrochloric acid. Here, depending on the substituent in position 4 of the thiazoline ring, it goes at different rates. Thus, substance (I) is converted to 2-phenylamino-4-methylthiazole (V) by boiling with 10% hydrochloric acid for several hours. Compound (V) was identified as that which we obtained according to Traumann from chloroacetone and phenylthiourea [3]. The rearrangement of compound (II) into 2-phenyl-4-phenylthiazole (VI) occurred after boiling for many days with hydrochloric acid. Substance (VI) was identical with that described by Beyer and synthesized from phenylthiourea and ω-bromoacetophenone [4].

For carrying out the rearrangement of compound (IV) into 2-phenylamino-4,5-cyclotetramethylenethiazole (VII) it was necessary to boil still longer with 20% hydrochloric acid. Compound (VII) has been obtained by Indian authors by condensation of cyclohexanone with phenylthiourea in the presence of iodine [5]. It is interesting to see that in the attempt to obtain this substance by condensation of α-chlorocyclohexanone with phenylthiourea substance (IV) was obtained, while according to the literature such a condensation of α-haloketones with 2-alkyl (aryl) thioureas leads to formation of 2-alkyl (aryl) aminothiazoles [6]. When substance (III) is boiled for four days in concentrated hydrochloric acid rearrangement into 2-phenylamino-4-p-nitrophenylthiazole occurs to about the extent of 15%. We identified the latter substance with that obtained from phenylthiourea and ω-bromo-p-nitroacetophenone.

The occurrence of these transformations shows that 2-imino-substituted 4-thiazolines (I, II, III, IV) when boiled with hydrochloric acid undergo rearrangement in which there is a transfer of the phenyl from the nitrogen of the ring to the exocyclic nitrogen.



Found %: C 60.50; H 3.88; N 14.03; S 11.02. $C_{15}H_{11}O_2N_3S$. Calculated %: C 60.85; H 3.72; N 14.12; S 10.78.

The picrate of (VIII) appeared as yellow fibrous crystals (from alcohol) m.p. 198-199° (decomposition), soluble in most organic solvents, insoluble in water.

Found %: N 15.86. $C_{15}H_{11}O_2N_3S \cdot C_6H_3O_7N_3$. Calculated %: N 15.9.

Action of hydrochloric acid on 2-imino-3-phenyl-4-p-nitrophenyl-4-thiazoline (III) and on 2-benzoylimino-3-phenyl-4-p-nitrophenyl-4-thiazoline. To 0.7 g of (III) was added 20 ml of concentrated hydrochloric acid. The orange color of the base changed to the yellow of the hydrochloride. The suspension was boiled for 37 hours. The yellow precipitate which appeared on cooling was filtered off. Evaporation of the hydrochloric acid mother liquor gave a further amount of hydrochloride. The yellow precipitate of the salt was washed repeatedly with water, and the precipitate which remained on the filter became orange. We obtained 0.11 g of substance which after recrystallization from alcohol consisted of needles. m.p. 208.5-210°. A sample mixed with (VIII) obtained by the above method gave no melting point depression.

The wash water was made alkaline with ammonia and evolved 0.45 g of an orange precipitate; triangular plates from alcohol, m.p. 156-158°. A sample mixed with (III) gave no melting point depression.

When 2-benzoylimino-3-phenyl-4-p-nitrophenyl-4-thiazoline was boiled in concentrated hydrochloric acid for two days it also evolved a mixture of 2-phenylamino-4-p-nitrophenylthiazole and 2-imino-3-phenyl-4-p-nitrophenyl-4-thiazoline.

Action of hydrochloric acid on 2-acetylimino-3-phenyl-4,5-cyclotetramethylene-4-thiazoline and on 2-imino-3-phenyl-4,5-cyclotetramethylene-4-thiazoline (IV). A solution of 1.36 g of 2-acetylimino-3-phenyl-4,5-cyclotetramethylene-4-thiazoline in 10 ml of 20% hydrochloric acid was boiled for 130 hours after which the reaction mass was evaporated, the residue dissolved in water, and the base precipitated by ammonia. The large colorless crystals on the filter deliquesced into a caramel-like substance which was a mixture of (IV) and (VII). For the isolation of the individual substances we used fractional precipitation of the picrates. In the first fraction we obtained the picrate of 2-phenylamino-4,5-cyclotetramethylene-4-thiazoline as yellow prisms (from alcohol), m.p. 201-202°.

Found %: C 49.94; H 3.73; N 14.92; S 6.93. $C_{13}H_{14}N_2S \cdot C_6H_3O_7N_3$. Calculated %: C 49.8; H 3.71; N 14.2; S 7.00.

The later fraction was the picrate of 2-imino-3 phenyl-4,5-cyclotetramethylene-4-thiazoline which was almost insoluble in alcohol. After recrystallization from acetic acid, needles with m.p. 228-230° (decomposition).

Found %: N 15.12. $C_{13}H_{14}N_2S \cdot C_6H_3O_7N_3$. Calculated %: N 15.2.

A mixed sample of this picrate with the picrate obtained from 2-imino-3-phenyl-4,5-cyclotetramethylenethiazoline described in the previous work [1] gave no melting point depression. The same picrate was isolated after boiling 0.69 g of 2-imino-3-phenyl-4,5-cyclotetramethylene-4-thiazoline with 7 ml of 20% hydrochloric acid for 90 hours.

2-Imino-3-phenyl-4,5-cyclotetramethylene-4-thiazoline (IV). A suspension of 1.52 g of phenylthiourea and 2 g of α-chlorocyclohexanone in 25 ml of anhydrous alcohol was boiled for two hours. The solution was evaporated dry and the residue was treated with water and ether. The water layer was made alkaline with ammonia and extracted with ether. After drying the ether extract it was evaporated and the residue was treated with dry ether in which part of the substance (0.25 g) did not dissolve. This was phenylthiourea which had not reacted. The ether solution was evaporated and the residue was recrystallized from 50% alcohol. We obtained 0.7 g of substance with m.p. 114-116°; after recrystallization from alcohol, colorless rectangular prisms, m.p. 117-119°, easily soluble in most organic solvents, insoluble in water. A sample mixed with imine (IV) obtained by saponification of 2-acylimino-3-phenyl-4,5-cyclotetramethylenethiazoles in aqueous alcoholic solution [1] gave no melting point depression. The picrate was also identical, m.p. 228-230° (decomposition).

SUMMARY

In a number of examples it has been shown that when substituted 2-imino-3-phenyl-4-thiazolines are boiled with hydrochloric acid, they are rearranged into the corresponding 2-phenylaminothiazoles, and a mechanism for this transformation has been suggested.

This rearrangement of the substituted 3-phenylthiazolone-2-imides can be explained as follows. Under the action of hydrogen chloride there occurs formation of a salt with addition of a proton to the nitrogen of the ring, due to which there is a decrease in strength of the 3,4 bond, and this bond is ruptured with polarization of the molecule at C_4 and the nitrogen of the imino group. A bond is formed between these atoms with formation of the substituted 2-phenylaminothiazole.

EXPERIMENTAL

2-Phenylamino 4-methylthiazole (V). A suspension of 1.52 g of phenylthiourea and 1.85 g of chloroacetone in 40 ml of alcohol was boiled with stirring for one hour. The solution was evaporated dry and the residue was treated with water, then made alkaline with ammonia and extracted several times with ether. After drying and distillation of the ether we obtained 1.75 g of a substance easily soluble in most organic solvents, insoluble in water. After recrystallization from alcohol, colorless needles with m.p. 116.5-118° (According to the literature [3]: m.p. 115-117° and 117-118°).

Action of hydrochloric acid on 2-benzoylimino-3-phenyl-4-methyl-4-thiazoline. A solution of 0.15 g of 2-benzoylimino-3-phenyl-4-methyl-4-thiazoline in concentrated hydrochloric acid was boiled for ten hours. Sublimation of benzoic acid was observed, and after cooling the reaction mass 0.05 g of this was isolated and identified. We isolated from the mother liquor with bicarbonate 0.08 g of substance with m.p. 115-117°. A sample mixed with substance (V) obtained by the method described above gave no depression of the melting point. When the water mother liquors were later made alkaline with ammonia we isolated 0.01 g of a white crystalline substance with m.p. 84-86°, identical with 2-imino-3-phenyl-4-methylthiazoline described in the preceding work [4].

2-Imino-3-phenyl-4-methyl-4 thiazoline picrate consisted of yellow prisms (from alcohol), m.p. 197.5-199° (decomposition), soluble in acetone, ethyl acetate, alcohols, more difficultly so in ether, insoluble in water.

Found %: N 16.58. $C_{10}H_{10}N_2S \cdot C_6H_3O_7N_3$. Calculated %: N 16.63.

Action of hydrochloric acid on 2-imino-3-phenyl-4-methyl-4-thiazoline (I). A solution of 0.29 g of (I) in 10 ml of 10% hydrochloric acid was boiled for nine hours. After cooling the reaction mass we isolated with ammonia 0.27 g of a white crystalline substance with m.p. 114-116°. After recrystallization from aqueous alcohol, needles with m.p. 117-118°. A sample mixed with substance (V) gave no depression of the melting point.

The picrate consisted of yellow needles (from alcohol), m.p. 209-210°, more difficultly soluble in organic solvents than the picrate of 2-imino-3-phenyl-4-methyl-4-thiazoline.

Found %: C 45.86; H 3.17; N 16.58; S 7.73. $C_{10}H_{10}N_2S \cdot C_6H_3O_7N_3$. Calculated %: C 45.9; H 3.1; N 16.63; S 7.67.

Action of hydrochloric acid on 2-imino-3,4-diphenyl-4-thiazoline (II). A solution of 0.2 g of substance (II) in 40 ml of 20% hydrochloric acid was boiled for 150 hours. After treatment with charcoal and distillation of the solvent the reaction mass was made alkaline and extracted with ether. From the dried ether extract we obtained 0.18 g of 2-phenylamino-4-phenyl-4-thiazoline (VI), needles (from alcohol): m.p. 136-138°. According to the literature [4], m.p. 139-140°, 138°. There is no depression of the melting point with the substance obtained by condensation of phenylthiourea with ω-bromoacetophenone (according to Beyer).

Substance (VI) was converted to the picrate, light yellow needles (from alcohol), m.p. 181-182° which agreed with the literature [7]. A sample mixed with the picrate of 2-phenylamino-4-phenylthiazole obtained according to Beyer also gave no melting point depression.

Found %: N 14.25. $C_{15}H_{12}N_2S \cdot C_6H_3O_7N_3$. Calculated %: N 14.5.

2-Phenylamino-4-p-nitrophenylthiazole (VIII). To a suspension of 1.52 g of phenylthiourea in 25 ml of alcohol was added with stirring 3 g of ω-bromo-p-nitroacetophenone in 25 ml of alcohol. The reaction mass grew warm, the white phenylthiourea dissolved, and a yellow precipitate appeared: 2 phenylamino-4-p-nitrophenylthiazole hydrobromide. After 15 minutes heating to boiling, the reaction mass was cooled, and the precipitate of hydrobromide was filtered off and washed with alcohol. When treated with water it hydrolyzed with formation of the orange base (VIII) (2.77 g, and 0.2 g from the mother liquor). After recrystallization from acetic acid we obtained 2.58 g (87.2%) of substance (VIII) with m.p. 209-210°; easily soluble in methylene chloride, ethyl acetate and acetone. It crystallized from alcohol in fibrous needles.

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*Original Russian pagination. See C. B. translation.

SYNTHESIS AND REARRANGEMENTS IN THE THIAZOLINIMINE SERIES

IV. ACTION OF ACETYLATING AGENTS ON 2-ACYLIMINO-4-HYDROXYTHIAZOLIDINES

K. M. Murav'eva and M. N. Shchukina

S. Ordzhonikidze All-Union Chemicopharmaceutical Scientifical Research Institute

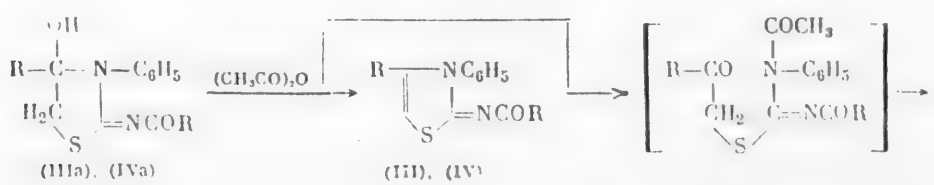
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2344-2348,
July, 1960
Original article submitted June 26, 1959

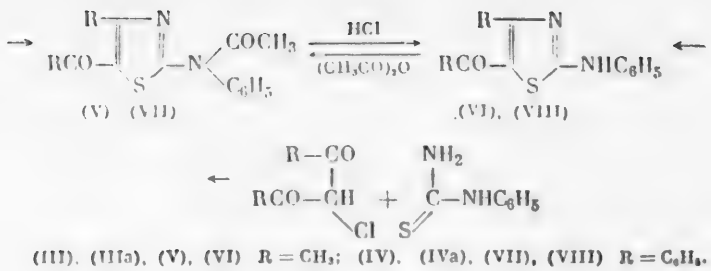
In previous communications [1, 2] we showed that 2-acylimino-3-phenyl-4-substituted 4-thiazolines are formed through the corresponding 4-hydroxythiazolidine derivatives. As intermediate products we isolated such hydroxy derivatives as 2-benzoyl- (Ia), 2-p-nitrobenzoyl-(IIa), and 2-acetyl-(IIIa) imino-3-phenyl-4-methyl-4-hydroxythiazolidines and 2-benzoylimino-3,4-diphenyl-4-hydroxythiazolidine (IVa).

In the present work we investigated the action of acetyl chloride and acetic anhydride on these hydroxythiazolidine compounds. It was found that O-acetylation did not occur. The action of acetic anhydride or acetyl chloride on compounds (Ia) and (IIa) eliminated a water molecule and formed 2-benzoylimino-3-phenyl-4-methyl-4-thiazoline (I) and 2-p-nitrobenzoylimino-3-phenyl-4-methyl-4-thiazoline (II). The structure of compounds (I) and (II) was demonstrated by their synthesis [1] from chloroacetone and the corresponding N-phenyl-N'-acetylthioureas.

When the hydroxythiazolidine derivative (IIIa) was heated with acetic anhydride, the reaction proceeded in two directions. Together with the elimination of a water molecule and the formation of 2-acetylimino-3-phenyl-4-methyl-4-thiazoline (identical with that obtained from chloroacetone and N-phenyl-N'-acetylthiourea [1]) there was formed 2-(N-phenyl-N-acetyl) amino-4-methyl-5-acetylthiazole (V), which was shown to contain a keto group by means of the infrared spectrum. When heated with hydrochloric acid, compound (V) was hydrolyzed with the formation of 2-phenylamino-4-methyl-5-acetylthiazole (VI), which gave a characteristic reaction for a keto group with dinitrophenylhydrazine. The structure of compound (VI) was demonstrated by synthesis [1] from diacetylchloromethane [3] and phenylthiourea.

An analogous conversion occurred with compound (IVa), which, on treatment with acetic anhydride and also acetyl chloride, lost a water molecule and formed 2-benzoylimino-3,4-diphenyl-4-thiazoline (IV), which we also obtained by condensation of ω-bromoacetophenone with N-phenyl-N'-benzoylthiourea [1], and 2-(N-phenyl-N-acetyl) amino-4-phenyl-5-benzoylthiazole (VII), which was shown to contain a keto group by the infrared spectrum. Substance (VII) was hydrolyzed with 20% hydrochloric acid to form 2-phenylamino-4-phenyl-5-benzoylthiazole (VIII). The structure of the latter was demonstrated by synthesis from phenylthiourea and dibenzoylchloromethane, which was obtained by chlorination of dibenzoylmethane with sulfuryl chloride in analogy with the chlorination of acetylacetone [3]. Compounds (VI) and (VIII) were acetylated by acetic anhydride to compounds (V) and (VII).

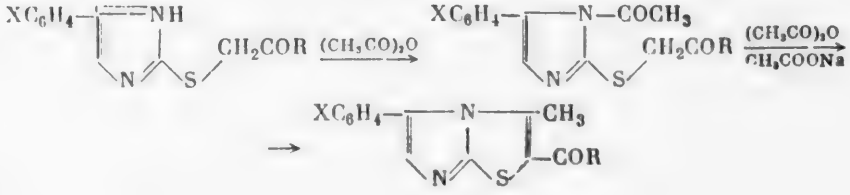




(III), (IIIa), (V), (VI) R = CH_3; (IV), (IVa), (VII), (VIII) R = C_6H_5.

These conversions apparently may be explained in the following way. The action of acetic anhydride on substances (IIIa) and (IVa) produced opening of the thiazolidine ring at the 3—4 bond with the formation of S-β-keto derivatives of isothiourea and acetylation of the secondary amino group. In these intermediate keto compounds, the hydrogen atoms of the methylene group have a high lability and readily react with the carbonyl of the acyl residue on the imino group to form compounds (V) and (VII). We observed this reactivity of the methylene group in S-β-keto derivatives of isothiourea in the formation of 2-phenylamino-4-methyl-5-acetylthiazole from N-phenyl-N'-acetylthiourea and chloroacetone in alcohol in the presence of triethylamine [1].

This peculiar closure of the thiazole ring, which involves elimination of a water molecule at the expense of the hydrogen atoms of the methylene group between the sulfur and the carbonyl group and the oxygen of the N-acetyl residue, was described by P. M. Kochergin for the formation of 3-methylimidazo-(2,1-b)-thiazolyl-2-alkyl (aryl) ketones from N-acetyl derivatives of 2-β-ketoalkyl (aryl)-mercaptoimidazoles [5].



EXPERIMENTAL

1. 2-Benzoylimino-3-phenyl-4-methyl-4-thiazoline (I). To a solution of 1.25 g of 2-benzoylimino-3-phenyl-4-methyl-4-hydroxythiazolidine in 8 ml of pyridine at 50° was added 0.3 ml of acetyl chloride. The reaction mixture was heated at 40-50° for 3 hr. The precipitate was collected and washed with benzene, ether, and water and had m.p. 156-158°. A mixed sample (from alcohol) with 2-benzoylimino-3-phenyl-4-methyl-4-thiazoline obtained by condensation of chloroacetone with N-phenyl-N'-benzoylthiourea [1] did not show depression of melting point. Compound (I) could also be obtained by boiling compound (I) with acetic anhydride and by recrystallization of the latter from acetic acid.

2. 2-p-Nitrobenzoylimino-3-phenyl-4-methyl-4-thiazoline (II). To 1.79 g of 2-p-nitrobenzoylimino-3-phenyl-4-methyl-4-hydroxythiazolidine was added 5 ml of acetic anhydride. The reaction mixture was boiled until darkening began. The precipitate was filtered from the cooled mixture and washed with ether. We obtained 1.23 g of a substance with m.p. 181-183°. A mixed melting point with 2-p-nitrobenzoylimino-3-phenyl-4-methyl-4-thiazoline obtained by condensation of chloroacetone with N-phenyl-N'-p-nitrobenzoylthiourea [1] was not depressed. A further amount of substance (II) was isolated from the mother solution. Substance (II) was also obtained by the reaction of compound (IIa) with acetyl chloride and also by recrystallization of (IIa) from acetic acid.

3. Action of acetic anhydride on 2-acetylimino-3-phenyl-4-methyl-4-hydroxythiazolidine (IIIa). To 1.25 g of 2-acetylimino-3-phenyl-4-methyl-4-hydroxythiazolidine was added 5 ml of acetic anhydride. The reaction mixture was heated until the solution darkened. The precipitate was filtered from the cooled mixture and washed with ether. We obtained 0.5 g of 2-(N-phenyl-N-acetyl) amino-4-methyl-5-acetylthiazole (V). By pouring the mother solution into water, we isolated a further 0.21 g of substance (V). The pearly, hexagonal platelets had m.p. 174-175° (from 50% CH_3COOH) and were soluble in methylene chloride, ethyl acetate, dichloroethane, benzene, and alcohols, less soluble in ether, and insoluble in water.

Found %: C 61.61; H 5.20; N 10.27; S 11.80. $C_{14}H_{14}O_2N_2S$. Calculated %: C 61.5; H 5.2; N 10.22; S 11.65.

Evaporation of the aqueous acetic acid mother solution in vacuum and recrystallization of the residue from aqueous acetic acid and then from alcohol yielded 0.23 g of colorless crystalline prisms, aggregated in nodules, with m.p. 182-183°. A mixed melting point with 2-acetylimino-3-phenyl-4-methyl-4-thiazoline (III) obtained by condensation of N-phenyl-N'-acetylthiourea with chloroacetone [1] was not depressed.

4. 2-Phenylamino-4-methyl-5-acetylthiazole (VI). A solution of 0.16 g of 2-(N-phenyl-N-acetyl) amino-4-methyl-5-acetylthiazole was boiled in 20% hydrochloric acid for 3.5 hr. The reaction mixture was then evaporated to colorless substance (VI), which was readily soluble in most organic solvents and insoluble in water; it had m.p. 152-153° (from alcohol). A mixed melting point with 2-phenylamino-4-methyl-5-acetylthiazole obtained by condensation of phenylthiourea with diacetylchloromethane [1] was not depressed.

5. Acetylation of 2-phenylamino-4-methyl-5-acetylthiazole (VI). A mixture of 2.32 g of 2-phenylamino-4-methyl-5-acetylthiazole and 9.3 ml of acetic anhydride was heated on a boiling water bath for 9 hr. The precipitate was filtered from the cooled mixture and washed with ether. We obtained 2.46 g of 2-(N-phenyl-N-acetyl) amino-4-methyl-5-acetylthiazole with m.p. 173-174°. A further 0.26 g of the substance was isolated from the mother solution. Recrystallization from alcohol or acetic acid yielded pearly platelets with m.p. 174-175°. A mixed melting point with the acetylation product of 2-phenylamino-4-methyl-5-acetylthiazole obtained from phenylthiourea and diacetylchloromethane [1] was not depressed.

6. Action of acetic anhydride on 2-benzoylimino-3,4-diphenyl-4-hydroxythiazolidine (IVa). To 1.12 g of 2-benzoylimino-3,4-diphenyl-4-hydroxythiazolidine was added 6 ml of acetic anhydride. The reaction mixture was heated on a boiling water bath with stirring for 1.5 hr. The dark mixture was poured into water. The precipitate was collected and washed with water. We obtained 1.11 g of a substance, which was recrystallized twice from acetic acid to give colorless prisms of 2-(N-phenyl-N-acetyl)-amino-4-phenyl-5-benzoylthiazole (VII) with m.p. 197.5-198.5°; the substance was soluble in methylene chloride, dichloroethane, chloroform, dioxane, benzene, and ethyl acetate, less soluble in alcohols and ether, and insoluble in ligroin and water.

Found %: C 72.84; H 4.67; N 7.01; S 7.99. $C_{24}H_{18}O_2N_2S$. Calculated %: C 72.6; H 4.53; N 7.05; S 8.07.

A mixed melting point with compound (VII) obtained by acetylation of 2-phenylamino-4-phenyl-5-benzoylthiazole which was prepared by condensation of dibenzoylchloromethane with phenylthiourea was not depressed.

From the acetic acid mother solution from the first recrystallization we isolated a precipitate of long, colorless needles with m.p. 203-204° (from alcohol). The substance dissolved in most organic solvents, but not in water. A mixed melting point with 2-benzoylimino-3,4-diphenyl-4-thiazoline obtained by condensation of N-phenyl-N'-benzoylthiourea with ω-bromoacetophenone [2] was not depressed. Compound (VII) was also obtained by the reaction of compound (IVa) with acetyl chloride.

7. Dibenzoylchloromethane. To a solution of 6.72 g of dibenzoylmethane [6] in 20 ml of anhydrous benzene, stirred at room temperature, was added 3 ml of sulfuryl chloride. The reaction mixture was stirred for 5 hr. After removal of the solvent in vacuum, the solid residue was recrystallized three times from methanol. Dibenzoylchloromethane was isolated as needles with m.p. 87-88° [4].

8. 2-Phenylamino-4-phenyl-5-benzoylthiazole (VIII). a) From 2-(N-phenyl-N-acetyl)amino-4-phenyl-5-benzoylthiazole (VII). A solution of 0.42 g of 2-(N-phenyl-N-acetyl) amino-4-phenyl-5-benzoylthiazole in 60 ml of 20% hydrochloric acid was boiled for 26 hr. The precipitate was collected and washed with water. Compound (VIII) was obtained as square platelets with m.p. 196.5-197.5° (from alcohol), which were readily soluble in most organic solvents and insoluble in water. A mixed melting point with 2-phenylamino-4-phenyl-5-benzoylthiazole obtained by condensation of dibenzoylchloromethane with phenylthiourea was not depressed.

Found %: C 74.07; H 4.41; N 7.83; S 8.77. $C_{22}H_{16}ON_2S$. Calculated %: C 74.13; H 4.52; N 7.86; S 8.99.

b) From phenylthiourea and dibenzoylchloromethane. To a suspension of 0.76 g of phenylthiourea in 25 ml of anhydrous alcohol, stirred at room temperature, was added a solution of 1.39 g of dibenzoylchloromethane in 25 ml of alcohol. The solution was boiled for 3 hr. The reaction mixture was evaporated to dryness and the residue repeatedly extracted with water and then alcohol. We obtained 0.97 g of a colorless crystalline substance, which was recrystallized from alcohol and then benzene to yield prisms with m.p. 196.5-197.5°. A mixed melting point with substance (VIII) obtained by method (a) was not depressed.

SUMMARY

1. It was shown that when treated with acetic anhydride or acetyl chloride, 2-acylamino-3-phenyl-4-hydroxy-4-substituted thiazolidines lose water and are converted into the corresponding derivatives of 4-thiazoline.

2. It was found that in addition to the above reaction, some 4-hydroxythiazolidine compounds also undergo conversion to 5-acyl derivatives of thiazole under the action of acetylating agents. This is apparently explained by opening of the ring at the 3–4 bond with subsequent acetylation of the secondary amino group and cyclization of the intermediate S-β-keto compound formed.

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NEW METHODS OF SYNTHESIS OF ESTERS OF PHOSPHONIC AND THIOPHOSPHONIC ACIDS

XXXIV. ADDITION OF DIALKYLTHIOPHOSPHOROUS ACIDS AND ACID ESTERS OF ETHYL- AND PHENYLPHOSPHINIC ACIDS TO UNSATURATED HYDROCARBONS

A. N. Pudovik and I. V. Konovalova

Kazan State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2348-2352, July, 1960
Original article submitted July 6, 1959

We have shown previously that dialkylphosphorous acids combine with unsaturated hydrocarbons in the presence of peroxides or by irradiation with ultraviolet light [1]. The combination occurs by a chain radical mechanism.

In the present work we have studied the addition reaction of dialkylthiophosphorous acids and acid esters of substituted phosphinic acids. As the dialkylthiophosphorous acids we have used diethyl, di-n-propyl, diisopropyl, and di-n-butylthiophosphorous acids. As the esters of the phosphinic acids, we have used the methyl, ethyl, and butyl esters of ethylphosphinic acid, and the methyl and ethyl esters of phenylphosphinic acid. Addition was carried out with hydrocarbons of the aliphatic series, 1-heptene to 1-undecene, and also cyclohexene. The reaction took place with irradiation of the reaction mixture by a mercury-quartz lamp, or by heating in the presence of benzoyl peroxide.

In each case we obtained the same esters of alkylthiophosphonic, dialkylphosphinic, and alkylphenylphosphinic acids with yields of 40-65%. We suggest the following mechanism for the reactions:

1a $(RO)_2PSH + h\nu \longrightarrow (RO)_2PS\cdot + H\cdot$

1b $(RO)_2PSH + C_6H_5COO\cdot \longrightarrow C_6H_5COOH + (RO)_2PS\cdot$

2. $R-CH=CH_2 + (RO)_2PS\cdot \longrightarrow R-\underset{\displaystyle S}{\overset{|}{C}}H-CH_2-\overset{\displaystyle S}{\overset{\|}{P}}-(OR)_2$

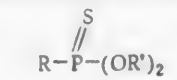
3. $R-\underset{\displaystyle S}{\overset{|}{C}}H-CH_2-P(S)(OR_2) + (RO)_2PSH \longrightarrow R-CH_2CH_2\overset{\displaystyle S}{\overset{\|}{P}}(OR)_2 +$
$+ (RO)_2PS\cdot$ etc.

4. $R-\underset{\displaystyle S}{\overset{|}{C}}H-CH_2-PS(OR)_2 + R-CH=CH_2 \longrightarrow$
$\longrightarrow (RO)_2P(S)CH_2-\underset{\displaystyle R}{\overset{|}{C}}H-CH_2-\underset{\displaystyle S}{\overset{|}{C}}H-R$ etc.

Reactions (1-3) describe the initiation, growth and formation of the reaction product; reaction (4) shows the formation of a polymeric residue due to further reaction of telomerization. The polymers are formed to the extent of 10-15% of the addition products. Dialkylphosphorous acid and the acid esters of phosphinic acids also combine with olefins in the absence of a catalyst, by heating the reagents at 135-140°. The addition compounds were prepared under conditions of irradiation, and in the presence of benzoyl peroxide. It should be noted that the starting reagents were used in the freshly distilled form, but no measures for the removal of oxygen and traces of peroxide were used. In the case of cyclohexene we compared the effect of the nature of the radicals in the dialkylthiophosphorous acids on the rate of the addition reaction. The rate at which the reaction occurred was characterized by the change in concentration of acid in the reaction mixture. It was shown that with increase of the radical the yield of phosphonic ester gradually and slowly decreased (see Fig. 1).

TABLE 1

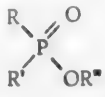
Alkythiophosphonic esters



No.	Meaning		Yield, %	B. p. (pressure in mm).	n_D^{20}	d_4^{20}	MR_D		P content, %	
	R	R'					Found	Calc.	Found	Calc.
1	C_5H_{11}	C_2H_5	61	116.5—117° (2)	1.4888	1.0577	64.49	64.54	13.20	13.13
2	C_7H_{15}	C_2H_5	60	146—148 (13)	1.4640	0.9800	70.94	71.34	11.99	12.3
3	C_8H_{17}	C_2H_5	60	164.5—165 (16)	1.4645	0.9721	75.54	75.96	11.82	11.65
4	C_9H_{19}	C_2H_5	30	173—174 (14)	1.4646	0.9635	80.39	80.58	11.18	11.07
5	$C_{10}H_{21}$	C_2H_5	54	185—186 (16)	1.4648	0.9590	84.78	85.20	10.56	10.54
6	$C_{11}H_{23}$	C_2H_5	50	197—198 (14)	1.4660	0.9558	89.25	89.81	10.23	10.06
7	C_8H_{17}	iso-C_3H_7	40	122—123 (1)	1.4560	0.9464	80.39	80.57	11.27	11.07
8	C_8H_{17}	iso-C_3H_7	53	165—165.5 (8.5)	1.4565	0.9409	84.96	85.20	10.73	10.54
9	C_9H_{19}	iso-C_3H_7	41	139—140 (1)	1.4585	0.9342	90.03	89.806	10.40	10.06
10	$C_{10}H_{21}$	iso-C_3H_7	72	150—151 (1)	1.4590	0.9305	94.59	94.42	9.83	9.62
11	C_6H_{11}	n-C_3H_7	44	129 (2)	1.4842	1.0234	73.82	73.87	11.74	11.74
12	C_7H_{15}	n-C_3H_7	43	146—147 (2)	1.4625	0.9485	81.19	80.68	10.60	11.07
13	C_9H_{19}	n-C_3H_7	38	148—148.5 (2)	1.4645	0.9444	89.91	89.93	10.20	10.06
14	C_6H_{11}	n-C_4H_9	58	141—142.5 (2)	1.4837	1.0026	83.32	83.21	10.90	10.61
15	C_7H_{15}	n-C_4H_9	35	161 (3)	1.4622	0.9468	89.45	89.82	10.20	10.06
16	C_8H_{17}	n-C_4H_9	66	165—166 (2.5)	1.4638	0.9378	94.62	94.44	9.62	9.13
17	C_9H_{19}	n-C_4H_9	56	166—167 (1.5)	1.4630	0.9380	98.70	99.16	9.50	9.22

TABLE 2

Alkylphenyl and Dialkylphosphinic acids



No.	Meaning			Yield, %	B. p. (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		P content, %	
	R	R'	R''					Found	Calc.	Found	Calc.
1	C_6H_5	C_6H_{11}	C_2H_5	33	182—183° (10)	1.5288	1.1010	70.62	70.79	12.29	12.3
2	C_6H_5	C_7H_{15}	C_2H_5	45	192 (10)	1.4989	1.0085	78.00	77.61	11.52	11.56
3	C_6H_5	C_8H_{17}	C_2H_5	37	174—175 (2)	1.5000	1.0101	82.12	82.23	11.05	10.99
4	C_6H_5	C_9H_{19}	C_2H_5	60	187—188.5 (2)	1.4970	0.9922	87.24	86.84	10.55	10.47
5	C_6H_5	$C_{10}H_{21}$	C_2H_5	71	199—200 (5.5)	1.4920	0.9851	91.33	91.46	10.14	10
6	C_6H_5	C_8H_{17}	CH_3	35	180—182 (2)	1.5000	1.0163	81.62	82.23	10.96	10.99
7	C_2H_5	C_6H_{11}	C_2H_5	25	142—143 (11)	1.4705	1.0241	55.59	55.92	15.03	15.19
8	C_2H_5	C_7H_{15}	C_2H_5	57	147—148 (10)	1.4440	0.9350	62.53	62.74	14.15	14.09
9	C_2H_5	C_9H_{19}	C_2H_5	65	172 (12)	1.4460	0.9310	71.06	71.97	12.56	12.50
10	C_2H_5	C_6H_{11}	CH_3	40	126—127 (11)	1.4755	1.0471	51.07	51.30	16.50	16.31
11	C_2H_5	C_7H_{15}	C_4H_9	46	170—171 (13)	1.4460	0.9232	71.64	71.97	12.49	12.50

The esters of alkylthiophosphonic acids are colorless liquids with a characteristic odor, almost insoluble in water, easily soluble in alcohol, ether, benzene, dioxane, and carbon tetrachloride. Their characteristics are given in Table 1.

The esters of dialkylphosphinic and alkylphenylphosphinic acids are also colorless liquids with weak odors, insoluble in water and soluble in organic solvents. The data are given in Table 2. By saponification of these esters with hydrochloric acid we obtained the corresponding dialkylphosphinic and alkylphenylphosphinic acids. These were crystalline substances, poorly soluble in water, easily so in alcohol, ether, benzene, and dioxane. Their characteristics are given in Table 3.

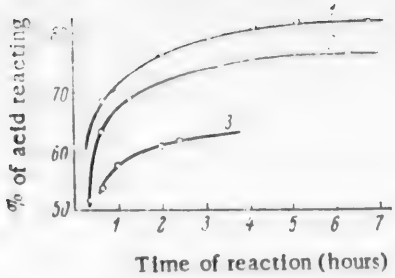


Fig. 1. Rate of reaction of cyclohexene in ultraviolet light with dialkylphosphorous acids. 1) Diethylthiophosphorous acid; 2) di-n-propylthiophosphorous acid; 3) di-n-butylthiophosphorous acid.

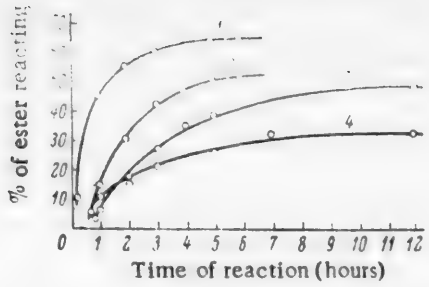
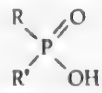


Fig. 2. Rate of reaction of 1-heptene with acid esters of phosphorus acids. 1) Diethylthiophosphorous acid; 2) acid ethyl ester of ethylphosphinic acid; 3) acid ethyl ester of phenylphosphinic acid; 4) diethylphosphorous acid.

The structure of one of the resulting compounds, the dibutyl ester of 1-heptylthiophosphorous acid, was shown by comparison of its constants and infrared spectrum with the analogous compound prepared from the counter synthesis by the Michaelis-Bekker reaction from sodium dibutylthiophosphite and normal heptyl iodide. Both products were entirely identical. On the basis of these results we have concluded that the addition of dialkylthiophosphorous acids to olefins on irradiation or in the presence of benzoyl peroxide occurs counter to the Markovnikov Rule.

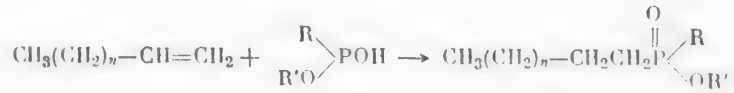
TABLE 3

Alkylphenyl- and Dialkylphosphinic acids



No.	Meaning		M.p.	Phosphorus content, %	
	R	R'		Found	Calculated
1	C_6H_5	C_6H_{11}	99—100.5°	13.70	13.83
2	C_6H_5	C_7H_{15}	40.5—41	13.06	12.91
3	C_6H_5	C_8H_{17}	40	12.49	12.20
4	C_6H_5	C_9H_{19}	39	11.49	11.56
5	C_6H_5	$C_{10}H_{21}$	55.5—56	10.81	10.78
6	C_2H_5	C_6H_{11}	59—60.5	17.50	17.61
7	C_2H_5	C_9H_{19}	35.5—36	14.00	14.09

The order of addition of acid esters of ethyl- and phenylphosphinic acids is considered in the case of reaction of the acid ester of phenylphosphinic acid and 1-heptene. The ethyl ester of 1-heptylphenylphosphinic acid was obtained by the Arbuzov rearrangement of the diethyl ester of phenylphosphinic acid in the presence of heptyl iodide. The constants of both products were very close. Heptylphenylphosphinic acid, obtained by saponification of both esters, had the same melting point. A mixed sample gave no melting point depression. This permits us to declare both products identical. We can conclude from these results that addition in this reaction also goes counter to the Markovnikov Rule.



In conclusion we carried out a comparison of the reactivity of a series of esters of phosphorus acids in the reaction of addition to olefins. Comparison was made of the rate of addition to 1-heptene of the acid ethyl esters of phosphorous, thiophosphorous, ethylphosphinic, and phenylphosphinic acids in ultraviolet light. From the degree of decrease in reactivity in this reaction, the esters could be arranged in the following order (see Fig. 2).

$$(C_2H_5O)_2PSH > C_2H_5P(O)(OC_2H_5)-H > C_6H_5P(O)(OC_2H_5)-H > (C_2H_5O)_2POH.$$

EXPERIMENTAL

The olefins with definite position of the double bond were synthesized by the reaction of allyl bromide with the corresponding magnesium organic compound [2]. We used freshly distilled reagents for the experiments.

Carrying out the addition reactions. a) An equimolecular mixture of dialkylthiophosphorous acids (or esters of phosphinic acids) and olefins were placed in a quartz flask and continuously illuminated with a mercury-quartz lamp PRK-2 placed at a distance of 5-6 cm for 5-8 hours at 85-90°.

b) An equimolecular mixture of reagents was heated under reflux on a glycerol bath in the presence of benzoyl peroxide for 20-25 hours. The temperature was kept at 80-85°. Several times during the reaction benzoyl peroxide was added in portions in the amount of 1% of the weight of reagents. The addition products were isolated from the reaction mixture by vacuum distillation.

Saponification of esters of dialkylphosphinic and alkylphenylphosphinic acids. The esters were heated with a 3-4 fold excess of 50% hydrochloric acid in a sealed tube at 150-160° for eight hours (the saponification reaction also took place well by heating 10-12 hours under reflux). Then the solution was slowly evaporated on the water bath to remove HCl and left for crystallization. For purification, the resulting crystals were dissolved in ether and boiled with animal charcoal. The final crystallization was carried out from ether.

Reaction of diethyl ester of phenylphosphinic acid with heptyl iodide. We heated 10.5 g of diethyl ester of phenylphosphinic acid (b.p. 113–115° at 15 mm, n_D^{20} 1.5115) and 14 g of heptyl iodide (b.p. 91° at 12 mm) in a sealed tube for nine hours at 140-160°. Then the reaction mixture was distilled in a vacuum. After several distillations we obtained 6.8 g of ethyl ester of 1-heptylphenylphosphinic acid.

B.p. 189–190° at 9 mm, n_D^{20} 1.4973, d_4^{20} 1.0072, MR_D 77.87; Calculated 77.61.

Found %: P 11.3. $C_{15}H_{25}O_2P$. Calculated %: P 11.56.

The constants of the ethyl ester of 1-heptylphenylphosphinic acid obtained by addition of the acid ethyl ester of phenylphosphinic acid to 1-heptene are given in Table 2 (substance 2).

Reaction of sodium dibutylthiophosphite with heptyl iodide. To an ether solution of sodium dibutylthiophosphite prepared from 14 g of dibutylthiophosphorous acid and 2 g of sodium was added with stirring 17.6 g of heptyl iodide. Then the mixture was heated on a water bath for three hours, treated with a small amount of water, and the ether layer was dried and distilled. After three vacuum distillations we obtained 5.7 g of the dibutyl ester of 1-heptylthiophosphorous acid.

B.p. 160–160.5° at 3 mm, n_D^{20} 1.4618, d_4^{20} 0.9460, MR_D 89.37; Calculated 89.82.

Found %: P 10.10, 10.20. $C_{15}H_{33}O_2PS$. Calculated %: P 10.06.

The constants of the dibutyl ester of 1-heptylthiophosphorous acid obtained by addition of dibutylthiophosphorous acid to 1-heptene are given in Table 1 (substance 15).

L. M. Nikitin took part in the experimental work.

SUMMARY

1. We have shown that dialkylthiophosphorous acids and acid esters of ethyl- and phenylphosphinic acids add to olefins in the presence of benzoyl peroxide or with illumination by ultraviolet light.

The addition products, esters of alkylthiophosphonic, dialkylphosphinic, and alkylphenylphosphinic acids, are obtained in yields of 40-65%.

2. Addition of dialkylthiophosphorous acids and acid esters of ethyl- and phenylphosphinic acids occurs by the radical mechanism, opposite to the Markovnikov Rule.

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2. B. A. Kazanskii et al., Zhur. Obshchei Khim. 17, 1507 (1947).

STUDIES IN THE FIELD OF HETEROCYCLIC CHEMISTRY. XXXIII. THE SYNTHESIS OF QUINAZOLONE COMPOUNDS ON THE BASIS OF ANTHRANILIC ACID ARYLAMIDES

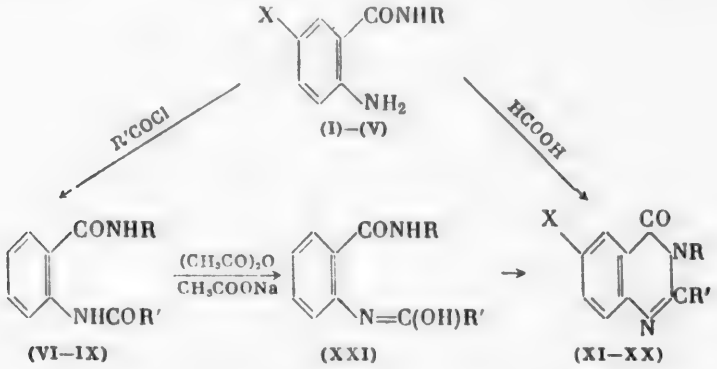
P. A. Petyunin and Yu. V. Kozhevnikov

Perm Pharmaceutical Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2352-2357, July, 1960
Original article submitted June 25, 1959

Recently there have been studies in the field of quinoline compounds for the purpose of obtaining effective antimalarials [1]. These investigations were evidently induced by the fact that the medicinal preparation Chanshan, obtained from the Chinese plant Dichroa febrifuga Lour., is 50-100 times more potent than quinine and contains a substance of the quinazolone series [2]. In this respect, there is the greatest interest in derivatives of 4-quinazolone with substituents in positions 3, and 2 and 3. The first are usually obtained by reaction of 4-quinazolone with alkyl halides in the presence of alcoholates [3] or by heating anthranilic acid with N-aryl (alkyl)-formamides [4, 5]; the second by heating N-acylanthranil with amines [6], in the reaction of N-arylbenzimidoyl chlorides with methyl anthranilate or with methyl esters of o-nitrobenzoic acids with later reduction [7, 8], or by heating amines with N-acylanthranilic acids in the presence of phosphorus trichloride [9].

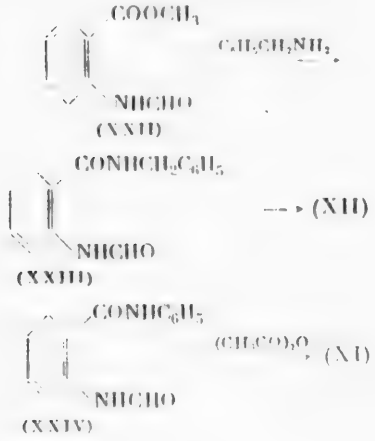
In connection with working out a satisfactory method of preparing aryl (alkyl) amides of anthranilic acid [10] we set ourselves the problem of working out a method based on these compounds for obtaining derivatives of 4-quinazolone with substituents in position 3, and 2 and 3.



The starting arylamides of anthranilic acid (I-V) are shown in Table 1.

3-Aryl substituted 4-quinazolones (XI-XV) were obtained in good yields by short heating of (I-V) with formic acid. Also, in the case of formation of (XII) and (XI) it was shown that for the synthesis of (XI-XV) we could use the reaction of aromatic amines with the methyl ester of N-formylanthranilic acid (XXII) and also closure of the quinazolone ring in the anilide of N-formylanthranilic acid (XXIV) with the help of acetic anhy-

hydride. It is true the first reaction goes less smoothly, and evidently it goes through the stage of formation of the benzylamide of N-formylanthranilic acid (XXIII).

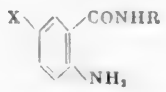


For the preparation of quinazolone compounds with substituents in positions 2 and 3 we tried unsuccessfully to carry out a reaction between (I-V) and different acids (R – COOH; R = CH_3, n-C_4H_9, iso-C_4H_9, $C_6H_5OCH_2$, and $(C_6H_5)_2CH$); the experiments were carried out at temperatures of the boiling acids, and in the case of the aromatic acids, at 180-230° for 3 hours; in the best case there was finally formed a trace of N-acylanthranilic acid; the easier closure of the quinazolone ring (in I-V) when formic acid takes part is probably explained by the fact that the intermediate product formed here, the N-formyl derivative of (I-V), is formed more easily than the other N-acyl derivatives and undergoes a lactam-lactim tautomerism. According to Orlov [11] arylamides of formic acid can exist in two tautomeric forms.

The synthesis of 2,3-disubstituted 4-quinazolones is possible on the basis of the arylamides of the N-acylanthranilic acids (VI-IX) (Table 2).

TABLE 1

Arylamides of Anthranilic Acid



Substance no.	Meaning X	Meaning R	Yield, %	M. p.	Form of crystals	Formula	Results of analysis for nitrogen (calculated values in parentheses), %
III	Cl	$C_6H_5CH_2$	57.4	146—147°	Needles	$C_{14}H_{13}ON_2Cl$	10.87, 10.70 (10.74)
IV	Br	$C_6H_5CH_2$	52.9	140—141	Needles	$C_{14}H_{13}ON_2Br$	9.04, 9.10 (9.18)
V	H		94	132—133	Platelets	$C_{12}H_{11}ON_3$	19.98, 19.60 (19.71)

Note: Crystallization was carried out from alcohol; the alcoholic solution of (V) had a weak blue fluorescence.

Under the action of acyl halides on the anilide (I) and benzylamide of anthranilic acid (II) we obtained (VI-IX) which when heated with acetic anhydride in the presence of anhydrous sodium acetate were transformed into the corresponding quinazolone compounds (XVI-XIX). We should mention that without sodium acetate, this transformation hardly occurs. It can be assumed that in the presence of sodium acetate enolization of the arylamide group (XXI) is facilitated, and hence also the closure of the quinazolone ring.

The quinazolone compound (XVI) can be obtained by direct heating of (I) with acetic anhydride in the presence of sodium acetate, without the stage of isolation of the anilide of the N-acetylanthranilic acid (VI). In the case of the anilide of N-benzoylanthranilic acid (X) the quinazolone ring is not closed in this case. This is probably connected with the very poor solubility of (X) in acetic anhydride. The conversion of (X) into 2,3-diphenyl-4-quinazolone (XX) can easily be carried out with benzoyl chloride. The structures and properties of the quinazolone compounds are given in Table 3.

EXPERIMENTAL

The benzylamides of 5-chloro-(III) and 5-bromo-(IV) anthranilic acid and the α-pyridylamide of anthranilic acid were obtained according to the data of [10].

TABLE 2

Arylamides of N-Acylanthranilic Acids

Substance No.	Meaning R	Meaning R′	Yield, %	Melting point	Solvent for crystallization	Form of crystals	Formula	Results of analysis (calculated values in parentheses), %
VII	C_6H_5	$C_6H_5OCH_2$	69	197—198°	Alcohol + acetone	Needles	$C_{21}H_{18}O_4N_2$	N 8.49, 8.03 (8.09)
VIII	C_6H_5	$(C_6H_5)_2CH$	77	202—203	Glacial acetic acid	Needles	$C_{27}H_{22}O_2N_2$	N 6.94, 7.02 (6.89)
IX	$C_6H_5CH_2$	$(C_6H_5)_2CH$	98	134—135	Alcohol	Needles collected in clumps	$C_{28}H_{24}O_2N_2$	C 79.75, 79.98 (80.00); H 5.73, 5.97 (5.71); N 6.67, 6.87 (6.66)

3-Phenyl-4-quinazolone (XI). a) Three g of substance (I) and 4.5 ml of 85% formic acid were boiled one hour and poured into 20 ml of water. The resulting precipitate was filtered, washed with 5% soda solution, then with water, and was crystallized. Yield 3 g. By process "a" we also obtained (XII), 3-benzyl-6-chloro-4-quinazolone (XIII), 3-benzyl-6-bromo-4-quinazolone (XIV), and 3-(α-pyridyl)-4-quinazolone (XV) (for (XV) the time of heating was 3 hours).

b) Three g of substance (XXIV) and 5 ml of acetic anhydride were boiled one hour, poured into 30 ml of water, and after hydrolysis of the acetic anhydride, the mixture was treated as in experiment "a". Yield 2.5 g of the substance described above which in a mixed m.p. gave no depression.

3-Benzyl-4-quinazolone (XII). We boiled 1.8 g of (XXII) and 1.1 g of benzylamine for five hours and after cooling the substance crystallized. Yield 1.4 g (42.5%). The substance mixed with a sample obtained by process "a" gave no melting point depression.

Anilide of N-phenoxyacetylanthranilic acid (VII). To a solution of 4.24 g of (I) in 10 ml of pyridine was added 3.4 g of phenoxyacetyl chloride. After standing for 10 min, it was poured into 50 ml of water, the precipitate was filtered, washed with dilute hydrochloric acid, water, and was crystallized. Yield 4.8 g.

In an analogous way we obtained (VIII) and (IX).

2-Methyl-3-phenyl-4-quinazolone (XVI). One g of substance (VI), 2 ml of acetic anhydride, and 0.3 g of freshly calcined sodium acetate were boiled for 1 hour on a sand bath and poured into 10 ml of water; the precipitate was filtered off, washed with 5% soda solution, with water, and was crystallized. Yield 0.8 g.

Analogous results were obtained if instead of (VI) we used (I). We also obtained 2-phenacyl-3-phenyl-4-quinazolone (XVII), 2-benzhydryl-3-phenyl-4-quinazolone (XVIII), and 2-benzhydryl-3-benzyl-4-quinazolone (XIX).

2,3-Diphenyl-4-quinazolone (XX). One g of (X) and 1 ml of benzoyl chloride were heated on a sand bath. When the precipitate had dissolved completely, boiling was continued for 5 minutes, the mixture was poured into water and the precipitate was treated in the usual way. Yield 1.2 g. Analogous results were obtained by heating (I) with benzoyl chloride.

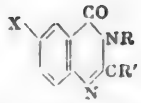
SUMMARY

1. Based on the arylamides of anthranilic acid we have worked out several variant methods for obtaining 3-aryl substituted 4-quinazolones.

2. We have shown that under the influence of acetic anhydride and anhydrous sodium acetate the arylamides of N-acylanthranilic acids are converted easily and in high yields into 2,3-disubstituted 4-quinazolones. In the case of the arylamides of N-benzoylanthranilic acid it is recommended to use benzoyl chloride as the cyclizing medium.

TABLE 3

4-Quinazolone Compounds



Substance No.	Meaning X	Meaning R'	Meaning R	Yield, %	Melting point	Crystal form	Formula	Results of analysis, % (calculated values in parentheses)
XI	H	H	C_6H_5	95	138—139° [4]	Needles	$C_{14}H_{10}ON_2$	—
XII	H	H	$C_6H_5CH_2$	77	117—118 [12]	Platelets	$C_{15}H_{12}ON_2$	—
XIII	Cl	H	$C_6H_5CH_2$	96	120	Needles	$C_{15}H_{11}ON_2Cl$	N 10.51, 10.29 (10.24)
XIV	Br	H	$C_6H_5CH_2$	94	131—132	Needles	$C_{15}H_{11}ON_2Br$	N 9.00, 8.87 (8.88)
XV	H	H		99	140	Needles	$C_{13}H_9ON_3$	C 69.89, 69.91 (69.95); H 3.98, 4.05 (4.04); N 19.10, 18.87 (18.83)
XVI	H	CH_3	C_6H_5	86	142—143 [13]	Platelets	$C_{15}H_{12}ON_2$	—
XVII	H	$C_6H_5OCH_2$	C_6H_5	79.4	130—132	Platelets	$C_{21}H_{16}O_2N_2$	C 76.56, 76.91 (76.83); H 4.98, 4.97 (4.87); N 8.26, 8.27 (8.54)
XVIII	H	$(C_6H_5)_2CH$	C_6H_5	77.5	122—123	Needles	$C_{27}H_{20}ON_2$	C 83.37, 83.28 (83.50); H 4.97, 5.04 (5.15); N 7.25, 7.38 (7.21)
XIX	H	$(C_6H_5)_2CH$	$C_6H_5CH_2$	76	103—104	Platelets	$C_{28}H_{22}ON_2$	C 83.29, 83.27 (83.29); H 5.51, 5.59 (5.47); N 6.90, 6.93 (6.96)
XX	H	C_6H_5	C_6H_5	90	158—159 [8]	Platelets	$C_{20}H_{14}ON_2$	—

Note. 1) Substance (XIV) was crystallized from methanol, the others from ethanol. 2) The dihydrochloride of (XV) was obtained by acidifying an alcoholic solution of the base with an alcoholic solution of hydrogen chloride needles melting about 250° (decomp.). Water and alcohol solutions of the salt are yellow. Found %: Cl 24.15, 24.03, $C_{13}H_9OH_3 \cdot 2HCl$. Calculated %: Cl 23.96.

3. We have obtained a series of previously undescribed arylamides of anthranilic acid, their N-acyl derivatives, and 3-and 2,3-substituted 4-quinazolones.

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SOME PROPERTIES OF ENOL ACETATES

V. VINYLATION OF CARBONYL COMPOUNDS

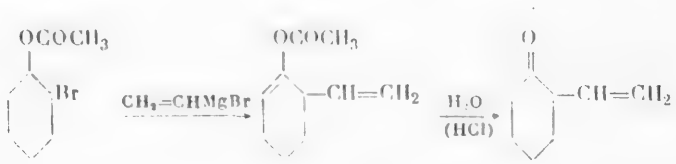
I. V. Machinskaya, V. A. Barkhash, and A. T. Prudchenko

D. I. Mendeleev Moscow Chemical Technological Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2357-2362, July, 1960
Original article submitted June 6, 1959

In the previous publication [1] we described a method for the alkylation of carbonyl compounds by the reaction between enol acetates substituted with bromine in the allyl position, and alkyl magnesium halides. In the present work we have determined that the reaction of enol acetates substituted with bromine with vinyl magnesium bromide leads to the vinylation of carbonyl compounds and to the formation from saturated aldehydes and ketones of γ, δ-, and in separate cases, of β,γ-unsaturated carbonyl derivatives of the ethylene series. The latter are rather difficult to prepare; we found only two general methods for their preparation in the literature, viz., heating esters of β-ketoacids and β,γ-ethylenic alcohols [2] leading to the formation of the corresponding γ,δ-unsaturated ketones, and carbonylation of hydrocarbons in the presence of $AlCl_3$ under pressure, leading to β,γ-unsaturated carbonyl compounds.

The following carbonyl compounds have now been vinylated: cyclohexanone, methyl ethyl ketone, methyl propyl ketone, benzylacetone, and butyraldehyde. The bromo-substituted enol acetates used acetone, and butyraldehyde. The bromo-substituted enol acetates used as starting materials were synthesized by us earlier by bromination of enol acetates with N-bromosuccinimide [1,4,5], with the exception of the bromo-substituted enol acetate of methyl ethyl ketone, viz., 1-bromo-acetoxy-2-butene, the preparation of which by a similar reaction is described in this paper*. Vinyl magnesium bromide was prepared by Norman's method [6] involving the reaction of magnesium with vinyl bromide in tetrahydrofuran medium. The reaction was carried out at the boiling point of the mixture; only in the case of the bromo-substituted cyclohexanone enol acetate, the reaction was carried out at -30° (because of the great unstability of the vinylation product). The reaction of the bromo-substituted enol acetate cyclohexanone with vinyl magnesium bromide gave the enol acetate of α-vinylcyclohexanone with a 52% yield. The free carbonyl compound was obtained by heating the enol acetate of α-vinylcyclohexanone with diluted hydrochloric acid; the yield of α-vinylcyclohexanone was 75.8%.



When vinyl magnesium bromide was made to react with the bromo-derivatives of enol acetates with the halogen atom in β-position with respect to the initial carbonyl group (of butyraldehyde, methyl ethyl ketone, and methyl propyl ketone), then the vinylation products were also obtained as enol acetates (with the respective yields of 45%, 49.5%, and 52%). Hydrolysis of the latter gave the corresponding γ,δ-unsaturated carbonyl com-

*In order to determine the position of bromine in this compound, we submitted it to ethylation with ethyl magnesium bromide which gave methyl butyl ketone. We thus show that by the reaction of the bromo-substituted enol acetate of methyl ethyl ketone with alkyl magnesium halides (by the alkylation method elaborated earlier [1]), one can obtain higher methyl ketones.

pounds: 3-methyl-4-pentene-1-aldehyde, 1-hexene-5-one, and 3-methyl-1-hexene-5-one in good yields. It is noteworthy that in distinction from the reaction of bromo-substituted enol acetates with alkyl magnesium halides which is accompanied by the splitting off of the enol acetate group, in the reaction with vinyl magnesium bromide, which we are describing now, no such regeneration of the carbonyl group is observed. This is apparently related to the lesser activity of vinyl magnesium compounds. Only in one case, viz., when vinylation was carried out on the bromo-substituted enol acetate of benzylacetone, a vinylation product with a free carbonyl group (3-phenyl-1-hexene-5-one) was actually formed (yield, 59%).

The isolated position of the double bonds in the vinylated enol acetates we are concerned with is confirmed by the following facts. A displacement of the double bond in the vinyl group would have led after hydrolysis to α, β-unsaturated carbonyl derivatives. However, the products we synthesized do not show in their ultraviolet spectra bands characteristic for such compounds. A displacement of the enol double bond is also to be excluded on the grounds that if this was the case, hydrolysis would have led in all the cases (except the enolate of α-vinylcyclohexanone) to the corresponding unsaturated alcohols, and not to the carbonyl compounds which are actually obtained. It is necessary to note that in his study of the reaction of allyl halides with vinyl magnesium bromide, Norman has always obtained the corresponding 1,4-dienes without any displacement of the double bonds to a conjugated position [7].

All the vinylated enol acetates and the corresponding carbonyl derivatives obtained by hydrolysis of these products (with the exception of 1-hexene-5-one) have not yet been described in the literature.

The results of this study show that the reaction of vinyl magnesium bromide with bromo-substituted enol acetates having the halogen atom in β-position with respect to the starting carbonyl group constitutes apparently a general method for the synthesis of γ, δ-unsaturated carbonyl compounds. In the case of α-bromo-substituted enol acetates (for instance, of the bromo-substituted enol acetate of cyclohexanone), the procedure we have elaborated leads to β,γ-unsaturated carbonyl compounds.

EXPERIMENTAL

1. α-Vinylcyclohexanone (by vinylation of the bromo-substituted enol acetate of cyclohexanone).

A. Enol acetate of α-vinylcyclohexanone. Vinyl bromide was prepared in a three-necked flask fitted with a stirrer, dropping funnel, and reflux condenser. The upper end of the condenser was connected through a series of wash-bottles to the dropping funnel of the apparatus set up for vinylation. A solution of 45 g of KOH in 225 ml of alcohol was put in the flask, and treated, with stirring, with 150 g of 1,2-dibromoethane. The flask was then slowly heated on a water bath to 80° while stirring (no water being circulated in the reflux condenser). The vinyl bromide thus formed was washed alcohol-free with tepid water, dried over calcium chloride, and adsorbed in 25 ml of tetrahydrofuran placed in the dropping funnel belonging to the apparatus set up for vinylation; during the absorption period, the dropping funnel was cooled with a mixture of solid carbon dioxide and alcohol.

Vinylation was carried out in a three-necked flask with a stirrer, a reflux condenser cooled with a mixture of dry ice and alcohol, and a stoppered dropping funnel cooled with the same cooling mixture. To the stopper of the dropping funnel was soldered a glass tube for the introduction of vinyl bromide, as well as a tube opened to the atmosphere and protected with a calcium chloride tube. The stem of the separating funnel was allowed almost to touch the bottom of the flask. Magnesium metal (4.25 g), tetrahydrofuran distilled first over KOH, and then over Na (100 ml), 2-3 ml of ethyl bromide and a few small crystals of iodine were introduced in the flask. Then, while stirring and heating to 40°, the solution of vinyl bromide in tetrahydrofuran was added to the reaction mixture. A violent reaction took place when nearly half of the solution had been added to the mixture; the flask was cooled with ice-cold water, while the remainder of the solution was introduced in the flask. After all the bromide had been added, the mixture was boiled for 30 min, then cooled to -30°, diluted with 100 ml of dry ether, and slowly treated with efficient stirring with a solution of 38 g of 2-bromo-1-acetoxy-1-cyclohexene* (b.p. 82-85° at 5 mm). The mixture was stirred for 12 hr at -30°, and decomposed with a saturated solution of NH_4Cl; the ethereal layer was separated out, the aqueous solution twice extracted with ether, and the combined ethereal extracts dried over Na_2SO_4. Ether and tetrahydrofuran were distilled off in vacuum. Vacuum distillation of the residue gave 1-acetoxy-1-cyclohexene (yield, 15.3 g, 53%).

*2-Bromo-1-acetoxy-1-cyclohexene was obtained by bromination of the enol acetate of cyclohexanone with N-bromosuccinimide [5].

B.p. 68–70° (2 mm), n_D^{20} 1.4[illegible], d_4^{20} 1.[illegible], MR_D [illegible]; Calculated [illegible].

Found %: C 72.12, 71.98; H 8.58, 8.65; Saponification number, 340.8; bromine number, 95.2. $C_{14}H_{24}O_2$. Calculated %: C 72.26; H 8.49. Saponification number 337.1; bromine number, 96.1.

B. Hydrolysis of the enol acetate of α-vinylcyclohexanone. Fifteen grams of the fraction boiling at 68-70° (2 mm) were heated with stirring with 200 ml of 4N HCl solution for 1 hr at 50-60° (water bath). The higher oily layer was separated out; the aqueous solution was neutralized with solid sodium carbonate and extracted with ether. The combined oily layer and ethereal extracts were washed with 15% Na_2CO_3 and water, and dried over sodium sulfate. Ether was removed by distillation, and the residue gave upon fractionation in vacuum 8.5 g of α-vinylcyclohexanone (75.8%).

B.p. 52–54° (2 mm), n_D^{20} 1.4907, d_4^{20} 0.995, MR_D 36.20; Calculated 36.49. Content of ketone, 99.6% (by preparation of oxime).

Found %: C 77.21, 77.13; H 9.89, 9.95. Bromine number, 125.9 $C_8H_{12}O$. Calculated %: C 77.37; H 9.74. Bromine number, 128.5.

2. 3-Methyl-1-hexene-5-one (by vinylation of the bromo-substituted enol acetate of methyl propyl ketone).

A. Enol acetate of 3-methyl-1-hexene-5-one. Norman's reagent was prepared from 12.2 g of Mg in 150 ml of anhydrous tetrahydrofuran, and a freshly prepared solution of 70.1 g of vinyl bromide in 125 ml of anhydrous tetrahydrofuran. The solution of vinyl magnesium bromide thus obtained was treated at -30° with a solution of 50.1 g of 4-bromo-2-acetoxy-2-pentene* (b.p. 46-48° at 4 mm) in 50 ml of absolute ether. The mixture was stirred at this temperature for 2 hr, and then left to stand overnight. On the next day the solution was boiled for 5 hr with stirring. The product was worked up in the same way as in the foregoing experiment. Vacuum distillation gave 19.4 g (52%) of 3-methyl-5-acetoxy-1,4-hexadiene.

B.p. 40-41° (50 mm), n_D^{20} 1.4111, d_4^{20} 0.859, MR_D 44.60; Calculated 44.48.

Found %: C 69.95, 70.05; H 9.35, 9.28. Saponification number, 358; bromine number, 98.2. $C_9H_{14}O_2$. Calculated %: C 70.10, H 9.15. Saponification number, 363; bromine number, 103.5.

B. Hydrolysis of the enol acetate of 3-methyl-1-hexene-5-one. Six grams of 3-methyl-5-acetoxy-1,4-hexadiene were heated with stirring with 100 ml of 4N HCl solution for 4 hr at a bath temperature of 50°. The mixture was worked up as described above. Vacuum distillation gave 3.14 g (72%) of 3-methyl-1-hexene-5-one.

B.p. 125–127°, n_D^{20} 1.4267, d_4^{20} 0.883, MR_D 32.65; Calculated 32.97. Content of ketone, 99.7% (by preparation of oxime).

Found %: C 74.76, 74.68, H 10.68, 10.81. Bromine number, 138.7. $C_7H_{12}O$. Calculated %: C 74.95; H 10.78. Bromine number, 142.5.

3. 3-Methyl-1-pentene-5-aldehyde (by vinylation of the bromo-substituted enol acetate of butyraldehyde).

A. Enol acetate of 3-methyl-1-pentene-5-aldehyde. Norman's reagent was prepared as usual from 12.2 g of Mg in 150 ml of anhydrous tetrahydrofuran, and a freshly prepared solution of 70.1 g of vinyl bromide in 125 ml of anhydrous tetrahydrofuran. The solution of vinyl magnesium bromide thus obtained was treated at -30°, and with stirring, a solution of 48.1 g of 2-bromo-4-acetoxy-3-butene** (b.p. 62-64° at 6 mm) in 50 ml of absolute ether was added. The mixture was stirred at this temperature for 2 hr, and then left to stand overnight. On the next day the solution was boiled with stirring for 4 hr. The usual treatment of the product and its fractionation in vacuum led to the separation of 15.7 g (45%) of 3-methyl-1-acetoxy-1,4-pentadiene.

B.p. 37–38° (10 mm), n_D^{20} 1.4123, d_4^{20} 0.887, MR_D 39.45; Calculated 39.86.

Found %: C 68.38, 68.28; H 8.95, 8.78. Saponification number, 387.2; bromine number, 112.5. $C_8H_{12}O_2$. Calculated %: C 68.54; H 8.63. Saponification number, 399.9; bromine number, 114.0.

*4-Bromo-2-acetoxy-2-pentene was obtained by bromination of the enol acetate of methyl propyl ketone with N-bromosuccinimide [4].

**2-Bromo-4-acetoxy-3-butene was obtained by bromination of the enol acetate of butyraldehyde with N-bromosuccinimide [1].

B. Hydrolysis of the enol acetate of 3-methyl-1-pentene-5-aldehyde. Five grams of 3-methyl-1-acetoxy-1,4-pentadiene was heated with stirring with 100 ml of a 2N HCl solution for 4 hr at the bath temperature of 50°. After the usual working up of the mixture, and distillation, 2.54 g (75.5%) of 3-methyl-4-pentene-1-aldehyde was obtained.

B.p. 110–112°, n_D^{20} 1.4082, d_4^{20} 0.868, MR_D 29.15; Calculated 29.45. Aldehyde content, 98.9% (by preparation of the oxime).

Found %: C 73.24; 73.18; H 10.35, 10.49. Bromine number, 158.5. $C_6H_{10}O$. Calculated %: C 73.42; H 10.27. Bromine number, 162.9.

4. 3-Phenyl-1-hexene-5-one (by vinylation of the bromo-substituted enol acetate of benzylacetone). Norman's reagent was prepared from 12.7 g Mg in 200 ml of tetrahydrofuran, and a freshly prepared solution of 72.9 g of vinyl bromide in 125 ml of tetrahydrofuran. The solution of vinyl magnesium bromide thus obtained was treated with a solution of 79.0 g of 1-bromo-3-acetoxy-1-phenyl-2-butene* (b.p. 122–124° at 2 mm) in 100 ml of ether at -30°. The reaction was carried out as in the foregoing experiment. Fractionation in vacuum gave 30.2 g (59%) of 3-phenyl-1-hexene-5-one.

B.p. 115–116° (5 mm), n_D^{20} 1.5112, d_4^{20} 0.979, MR_D 52.35; Calculated 53.56. Content of ketone, 99.8% (by preparation of oxime).

Found %: C 82.65, 82.59; H 8.35, 8.39. Bromine number, 93.5. $C_{12}H_{14}O$. Calculated %: C 82.71; H 8.10. Bromine number, 91.9.

5. 1-Hexene-5-one (by vinylation of the bromo-substituted enol acetate of methyl ethyl ketone).

A. Enol acetate of methyl ethyl ketone. One hundred grams of methyl ethyl ketone was dissolved in 430 g of acetic anhydride, and the mixture treated with 0.76 ml of concentrated sulfuric acid. After standing for 15 days at room temperature, the excess of acetic anhydride was decomposed by addition of ice and water with vigorous stirring during 30 min. The reaction mixture was then made weakly alkaline by the addition of solid sodium carbonate. The reaction product was then extracted with ether. The ethereal extract was washed with a saturated solution of sodium bisulfite, then with 15% aqueous sodium carbonate, and finally with water. After drying over sodium sulfate the ether was distilled off, and the residue fractionated in vacuum to give 116.9 g (73.5%) of 2-acetoxy-2-butene.

B.p. 32–34° (25 mm), n_D^{20} 1.4084, d_4^{20} 0.902, MR_D 31.30; Calculated 31.10.

Found %: C 63.05, 62.98; H 8.75, 8.97. Saponification number, 491.3; bromine number, 138.5. $C_6H_{10}O_2$. Calculated %: C 63.13; H 8.83. Saponification number, 490; bromine number, 134.0.

B. Bromination of the enol acetate of methyl ethyl ketone with N-bromosuccinimide. A mixture of 20 g of the enol acetate of methyl ethyl ketone, 31.25 g of N-bromosuccinimide, and 50 ml of CCl_4 was refluxed on a water bath. When the bath temperature reached 86°, a violent reaction occurred and all the N-bromosuccinimide which separated out was filtered off and washed with CCl_4. The combined filtrate and washings were repeatedly washed with water, and then dried over sodium sulfate. After removal of the solvent by distillation and vacuum fractionation of the residue, 12.7 g (37.6%) of 1-bromo-3-acetoxy-2-butene was obtained.

B.p. 31-32° (6 mm), n_D^{20} 1.4574, d_4^{20} 1.370, MR_D 38.46; Calculated 38.86.

Found %: Br 41.65; 41.54; saponification number, 578.5. $C_6H_9O_2Br$. Calculated %: Br 41.39. Saponification number, 580 (based on two equivalents of alkali, as the hydrolysis of the enol acetate group is accompanied by removal of HBr).

C. Enol acetate of 1-hexene-5-one. Norman's reagent was prepared from 6.9 g of Mg in 150 ml of tetrahydrofuran, and a freshly prepared solution of 40 g of vinyl bromide in 70 ml of tetrahydrofuran. The solution of vinyl magnesium bromide thus obtained was treated with 37 g of 1-bromo-3-acetoxy-2-butene at -30°. The mixture was boiled for 30 hr, and then worked up as in the preceding experiment. Vacuum fractionation gave 13.3 g (49.5%) of 2-acetoxy-2,5-hexadiene.

* 1-Bromo-3-acetoxy-1-phenyl-2-butene was obtained by bromination of the enol acetate of benzylacetone with N-bromosuccinimide [4].

B.p. 34–37° (35 mm); n_D^{20} 1.4331, d_4^{20} 0.918, MR_D 39.75; Calculated 39.86.

Found %: C 68.49, 68.35; H 8.71, 8.85. Saponification number, 392.5; bromine number, 110.9. $C_8H_{12}O_2$. Calculated %: C 68.54; H 8.63. Saponification number, 399.9; bromine number, 114.0.

D. Hydrolysis of the enol acetate of 1-hexene-5-one. Eight grams of 2-acetoxy-2,5-hexadiene was heated with stirring with 100 ml of 4N HCl solution for 3 hr at 60° in a bath. After the usual working up and distillation, 3.8 g (67.9%) of 1-hexene-5-one was obtained.

B.p. 126–127°, n_D^{20} 1.4221, d_4^{20} 0.856, MR_D 29.15; Calculated 29.45. Content of ketone 98.6% (by preparation of oxime)

Found %: C 73.38, 73.29; H 10.42, 10.39. Bromine number, 156.4. $C_6H_{10}O$. Calculated %: C 73.42; H 10.27. Bromine number, 162.9.

E. Reaction of the bromo-substituted enol acetate of methyl ethyl ketone with ethyl magnesium bromide. The Grignard reagent was prepared from 9.1 g of Mg, 45 g of C_2H_5Br, and 200 ml of ether; at the end of the reaction the mixture was heated on a water bath for 30 min at the boiling point of ether. The cooled solution of the reagent was added drop by drop, with vigorous stirring, to 51 g of 1-bromo-3-acetoxy-2-butene. The mixture was then heated for 20 hr on a water-bath at its boiling point. After usual procedure and vacuum fractionation, 12.4 g (47%) of methyl n-butyl ketone was obtained.

B.p. 39–41° (27 mm), n_D^{20} 1.4039, d_4^{20} 0.8170, MR_D 29.99; Calculated 29.92. Literature data [8]: b.p. 127–127.5°, d^{15} 0.8174. Content of ketone, 99.8% (by preparation of oxime).

Found %: C 71.83, 71.89; H 12.24, 12.39. $C_6H_{12}O$. Calculated %: C 71.95; H 12.08. Semicarbazone, m.p. 120–121° (from aqueous alcohol); literature data [8]: m.p. 118–121°.

Found %: N 26.54, 26.62. $C_7H_{15}ON_3$. Calculated %: N 26.73.

SUMMARY

1. A method is elaborated for the vinylation of carbonyl compounds in β-position (in the case of some ketones, in α-position) by the action of vinyl magnesium bromide on bromo-substituted enol acetates.

2. The reaction of bromo-substituted enol acetates of cyclohexanone, methyl ethyl ketone, methyl propyl ketone, and butyraldehyde with vinyl magnesium bromide gives the corresponding vinylated enol acetates with the respective yields of 53, 49.5, 52, and 45%. Hydrolysis of these compounds gives good yields of the corresponding unsaturated carbonyl compounds, viz., α-vinylcyclohexanone, 1-hexene-5-one, 3-methyl-1-hexene-5-one, and 3-methyl-4-pentene-1-aldehyde. The reaction of the bromo-substituted enol acetate of benzylacetone with vinyl magnesium bromide leads in one step to 3-phenyl-1-hexene-5-one with a 59% yield.

3. It is shown that N-bromosuccinimide reacts with the enol acetate of methyl ethyl ketone to give a 37.6% yield of 1-bromo-3-acetoxy-2-butene, which can give methyl ketones of more complicated structure by its reaction with alkyl magnesium halides.

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SOME PROPERTIES OF ENOLACETATES

VI. BROMO-SUBSTITUTED ENOLACETATES IN THE WURTZ-GRIGNARD REACTION

I. V. Machinskaya, V. A. Barkhash, and A. T. Prudchenko

D. I. Mendeleev Moscow Chemicotechnological Institute

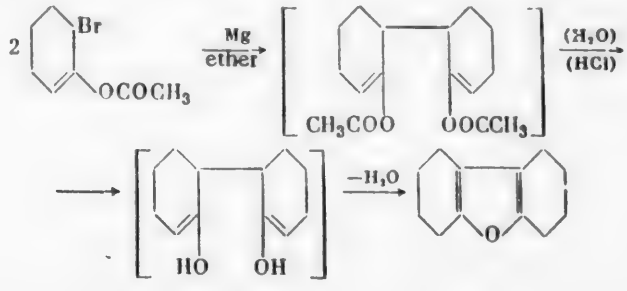
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2363-2366, July, 1960
Original article submitted July 6, 1959

In previous communications [1,2] we gave results of investigation of the reaction of enolacetates bromo-substituted in the allyl position with various organomagnesium compounds. In the present work we undertook the task of obtaining organomagnesium compounds from the same bromo-substituted enolacetates.

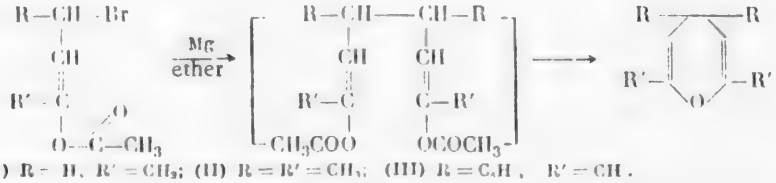
As is known, preparation of organomagnesium compounds from halogen-substituted ones with an allyl disposition of the halogen is difficult. Due to the mobility of the halogen the formation chiefly of compounds of the diallyl type occurs by the Wurtz reaction in this case. Gilman [3] succeeded in obtaining allyl organomagnesium compounds only by using an enormous excess of magnesium in the ratio 6:1 to the halogen derivative, at very high dilution. Recently, Rowlands and others [4] developed a special "cyclic reactor" for preparation of organomagnesium compounds of similar type, in which continuous recirculation of ether takes place, and the organomagnesium compound formed is immediately withdrawn from the sphere of reaction.

Our attempts to obtain organomagnesium compounds from bromo-substituted enolacetates of cyclohexanone, methyl ethyl ketone, methyl propyl ketone, benzylacetone, and butyric aldehyde under the reaction conditions recommended by Gilman, i.e. at high dilution (1:13), concluded unsuccessfully – bromo-substituted enolacetates did not react with magnesium. We were successful, however, in carrying out the reaction with the above enolacetates, using powdered magnesium activated by iodine, and carrying out the reaction with a concentrated solution of the halogen-substituted compound, which was quickly added to the magnesium in ether. To activate the process, periodic addition of iodine in ethyl bromide was carried out. At the conclusion of the reaction the mixture was acidified by hydrochloric acid, and the solution heated for several hours.

In the case of the brominated enolacetate of cyclohexanone, a 69% yield of symmetrical octahydrobenzofuran was obtained as the chief reaction product. Formation of this compound can be explained in the following manner. Bromo-substituted cyclohexanone enolacetate reacts with magnesium by the Wurtz reaction with formation of a diallyl type product which then hydrolyzeswith closing of a furan ring.



According to a similar scheme, evidently, proceeds the reaction with magnesium of bromo-substituted enolacetates of methyl ethyl ketone (I), methyl propyl ketone (II), and benzylacetone (III), in which the bromine atom occurs at the β-position to the carbonyl group. By reacting these bromoderivatives with magnesium under similar conditions, interesting unsaturated seven-membered heterocyclic compounds were obtained, not described in the literature. They were homologs of 4,5-dihydrooxepin: 2,7-dimethyl-(I), 2,4,5,7-tetramethyl-(II), and 2,7-dimethyl-4,5-diphenyl-4,5-dihydrooxepin (III), in yields of 68, 61.5, and 64.6% respectively.



(I) R = H, R′ = CH₃; (II) R = R′ = CH₃; (III) R = C₆H₅, R′ = CH₃.

The structure of the compounds obtained was confirmed by the data obtained from analyses of their reactions, and of their elements, and also by IR spectra.

It should be noted that recently interest has considerably increased in the chemistry of seven-membered unsaturated heterocyclic compounds which may possess aromatic properties similar to certain seven membered carbocyclic compounds (tropolones, azulenes). A dihydrooxepin ring has been observed in certain natural compounds. Thus, for instance, the alkaloid curalin proves to be substituted dibenzodihydrooxepin [5]. In 1958, Meinwald and Notzaki [6] synthesized 2,3,6,7-tetrahydrooxepin from butyl-3-ol. Homologs of dihydrooxepin, however, have not been obtained so far.

To confirm the scheme proposed for the reaction of bromo-substituted enolacetates with magnesium the data obtained on reacting with the bromo-substituted enolacetate of butyric aldehyde may be used: the originally formed product of the diallyl type proves to be so stable that, under the reaction conditions, it undergoes no further changes. Yield of the dienolacetate of 3,4-dimethylhexanedial-1,6, 47.2%. All efforts to saponify this product and achieve ring closure in this case did not lead to the desired result—the product was either not saponifiable at all, or resinification took place. This, evidently, is connected with the high stability of enolacetates of aldehydes compared with enolacetates of ketones.

IR-spectra were obtained at the optical department of the R. Grinberg Institute of Organic Chemistry of the USSR Academy of Sciences, to which the authors express their appreciation for this cooperation.

EXPERIMENTAL

1. 1,2,3,4,5,6,7,8-Octahydrodibenzofuran (from the bromo-substituted enolacetate of cyclohexanone). Into a three-necked flask, fitted with stirrer, reflux condenser, and dropping funnel, was introduced 15.6 g of powdered magnesium, this being then activated by heating with iodine. After cooling, 100 ml of absolute ether was added, then 1-2 ml of ethyl bromide and 2-3 ml of 2-bromo-1-acetoxycyclohexene-1 [7] added, whereupon a vigorous reaction began. Then dropwise, but rather quickly, was added with vigorous stirring a solution of 47 g of 2-bromo-1-acetoxycyclohexene-1 in 120 ml of absolute ether, whereupon the mixture boiled spontaneously. The solution was then boiled for a further 2 hours with stirring, then cooled and excess magnesium decomposed with a 4N HCl solution; the acid solution was boiled for 1.5 hours with stirring, cooled, extracted several times with ether, the ethereal extract washed with 15% soda solution, water, and dried with sodium sulfate. Ether was distilled off in vacuo without heating. By fractionating in vacuo, 13.1 g (69%) of octahydrodibenzofuran was isolated.

B. pt. 110–112° (2 mm), n_D^{20} 1.5127, d_4^{20} 1.0144, MR_D 52.09; Calc. 51.72.

Found %: C 81.45, 81.56; H 9.51, 9.43. Bromine number 182.4. $C_{12}H_{16}O$. Calculated %: C 81.77, H 9.15. Bromine number 181.2.

2. 2,7-Dimethyl-4,5-dihydrooxepin (from the bromo-substituted enolacetate of methyl ethyl ketone). In the reaction were used 26.1 g of powdered magnesium in 250 ml of ether and a solution of 69 g of 1-bromo-3-acetoxybutene-2 [2] in 50 ml of ether. Course of the reaction and treatment of products were as in the preceding experiment.

Yield 15.1 g (68%).

B. pt. 52–54° (10 mm), n_D^{20} 1.4298, d_4^{20} 0.891, MR_D 37.20; Calc. 37.65.

Found %: C 77.12, 77.05; H 9.98, 10.01. Bromine number 253.4. $C_8H_{12}O$. Calculated %: C 77.37; H 9.74. Bromine number 257.6.

IR-spectrum (cm^{-1}): 776, 852, 878, 902, 934, 967, 1005, 1048, 1077, 1123, 1176, 1252, 1371, 1445, 1613, 1691.

3. 2,4,5,7-Tetramethyl-4,5-dihydrooxepin (from the bromo-substituted enolacetate of methyl propyl ketone). In the reaction were used 19 g of powdered magnesium in 200 ml of ether and a solution of 53 g of 4-bromo-2-acetoxypentene-2 [8] in 50 ml of ether.

Yield 12 g (61.5%).

B. pt. 75–77° (7 mm). n_D^{20} 1.4487, d_4^{20} 0.879, MR_D 46.51; Calc. 46.89.

Found %: C 78.65, 78.72; H 10.70, 10.65. Bromine number 201. $C_{10}H_{18}O$. Calculated %: C 78.89; H 10.59. Bromine number 210.

IR-spectrum (cm^{-1}): 705, 751, 777, 888, 923, 962, 1056, 1098, 1133, 1175, 1206, 1232, 1383, 1457, 1618, 1681.

4. 2,7-Dimethyl-4,5-diphenyl-4,5-dihydrooxepin (from the bromo-substituted enolacetate of benzylacetone). In the reaction were used 13.3 g of powdered magnesium in 120 ml of ether and a solution of 73 g of 1-bromo-3-acetoxy-1-phenylbutene-2 [8] in 50 ml of ether.

Yield 24.2 g (64.6%).

B. pt. 104–106° (6 mm), n_D^{20} 1.5066, d_4^{20} 0.955, MR_D 85.30; Calc. 85.87.

Found %: C 86.85, 86.76; H 7.48, 7.52. Bromine number 110.5. $C_{20}H_{20}O$. Calculated %: C 86.92; H 7.29. Bromine number 115.6.

IR-spectrum (cm^{-1}): 695, 752, 778, 796, 814, 901, 933, 949, 994, 1030, 1077, 1097, 1156, 1291, 1333, 1361, 1412, 1455, 1493, 1596, 1612, 1649, 1705.

5. The Reaction of the Bromo-substituted Enolacetate of Butyric Aldehyde with Magnesium. In the reaction were used 12 g of powdered magnesium in 150 ml of ether and 33 g of 2-bromo-4-acetoxybutene-3 [1] in 25 ml of ether.

Yield 9.1 g (47.2%).

B. pt. 42–44° (7 mm), n_D^{20} 1.4044, d_4^{20} 0.9250, MR_D 59.99; Calc. 59.99.

Found %: C 63.51, 63.48; H 8.17, 8.31. Saponification value 492.8. $C_{12}H_{18}O_4$. Calculated %: C 63.69; H 8.00. Saponification value 495.

SUMMARY

1. It was shown that, on reacting magnesium in ether with bromo-substituted enolacetates of ketones possessing a halogen in the β-position relative to the carbonyl group, seven-membered unsaturated hydrogen-containing heterocyclic compounds are formed, being derivatives of 4,5-dihydrooxepin. Thus, from the bromo-substituted enolacetates of methyl ethyl ketone, methyl propyl ketone, and benzylacetone are obtained respectively by this reaction 2,7-dimethyl-4,5-dihydrooxepin (yield 68%), 2,4,5,7-tetramethyl-4,5-dihydrooxepin(yield 61.5%), and 2,7-dimethyl-4,5-diphenyl-4,5-dihydrooxepin (yield 64.6%).

2. It was found that the bromo-substituted enolacetate of cyclohexanone (with the halogen in the α-position to the carbonyl group) on reacting with magnesium in ether gives symmetrical octahydrodibenzofuran.

3. The bromo-substituted enolacetate of butyric aldehyde under similar conditions gives the dienolacetate of 3,4-dimethylhexanedial-1,6 by the Wurtz reaction.

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THE REACTION OF TETRAFLUOROETHYLENE WITH BORON TRICHLORIDE

Kh. R. Raver, A. B. Bruker, and L. Z. Soborovskii

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2366-2368, July, 1960
Original article submitted June 1, 1959

It is known that fluorine bonded to carbon can be substituted with chlorine by the action of aluminum chloride on carbon fluorides. Thus, on reacting benzotrifluoride with acetyl chloride in the presence of aluminum chloride, benzotrichloride and almost pure aluminum fluoride are obtained [1]. On reacting 1,1,2-trifluorotrichloroethane with aluminum chloride, formation of 1,1,1-trifluorotrichloroethane (50%) and 1,1-difluorotetrachloroethane (40%) takes place. Using aluminum chloride with a tagged chlorine atom in this reaction, radioactive chlorine was found in the difluorotetrachloroethane [2]. It has been shown that on reacting tetrafluoroethylene with arsenic trichloride in the presence of aluminum trichloride formation of difluorodichloroethylene takes place together with formation of pentafluoroethyldichloroarsine [3].

$$3CF_2{=}CF_2 + 2AsCl_3 \xrightarrow{AlCl_3} CF_3CF_2AsCl_2 + CF_2{=}CCl_2.$$

This unusual phenomenon was explained thus, that first of all interchange of halogens takes place between tetrafluoroethylene and aluminum trichloride. Then, on reacting tetrafluoroethylene with arsenic trichloride and aluminum difluoride chloride, formation of pentafluoroethyldichloroarsine takes place.

It has been established that on reacting aluminum trichloride with perfluoropropylene and 2-hydroperfluoropropylene in an acetyl chloride solution 2-fluoro and 2-hydroperchloropropylene are formed [4].

This fact, namely, that despite the high heat of reaction (107 kcal) fluorine is capable of being replaced by chlorine with formation of a C–Cl bond (66.5 kcal), is evidently connected with the fact that aluminum possesses a greater affinity for fluorine than for chlorine.

The reaction of tetrafluoroethylene with diborane and pentaborane has also been described [5, 6]. As a result of these reactions, formation of a series of compounds takes place, among them BF_3, $C_2H_5BF_2$, $(C_2H_5)_2BF$, i.e., substitution of hydrogen attached to boron by fluorine takes place.

In the present work the reaction of tetrafluoroethylene and boron trichloride was studied. It was expected that the boron chloride would, similarly to aluminum chloride, replace fluorine atoms by chlorine in carbon fluorides. Actually, on passing boron trichloride and tetrafluoroethylene vapors over carbon at 200–250°C, formation of boron trifluoride (which was isolated and identified as its etherate) and trichlorofluoroethylene takes place.

$$CF_2{=}CF_2 + BCl_3 \rightarrow CCl_2{=}CFCl + BF_3.$$

Similar results were obtained on reacting tetrafluoroethylene with boron trichloride in an autoclave under a pressure of 30–35 atm at 100–150°.

It should be noted that, unlike the reaction of tetrafluoroethylene with aluminum trichloride, in which difluorodichloroethylene and aluminum difluoride chloride are formed, in the reaction described by us formation of boron trifluoride and trichlorofluoroethylene takes place.

EXPERIMENTAL

1. Reaction of Tetrafluoroethylene with Boron Trichloride in a Tube over Carbon. Into a quartz tube (500 mm long and 30 mm in diameter) was placed 300 cm^3 (180.5 g) of dry activated carbon, and 406 g (3.4 mole) of boron trichloride and 170 g (1.7 mole) of tetrafluoroethylene were passed through for 8 hours at 200-250°. The reaction products were collected in collecting vessels connected in series, cooled with carbon dioxide; in the first collector, unreacted boron trichloride and trichlorofluoroethylene condensed, in the second collector, containing dry ether, boron trifluoride collected as its etherate. After several distillations of the contents of the first collector, besides unreacted boron trichloride (250 g), a fraction of amount 22.8 g was isolated, with b. pt. 69-70°, d_4^{20} 1.545, n_D^{20} 1.4280, in its constants and analytical data corresponding to trichlorofluoroethylene.

Data in the literature [7]: B. pt. 71°, d_4^{20} 1.546, n_D^{20} 1.4379.

Found %: C 16.87; F 12.65; Cl 71.72. C_2FCl_3. Calculated %: C 16.08; F 12.72; Cl 71.2.

After distillation of the ethereal solution, 38 g of the etherate of boron trifluoride was isolated.

B. pt. 126°, d_{20}^{20} 1.123, n_D^{20} 1.347.

Data in the literature [8]: B. pt. 125.7, d_4^{25} 1.125, n_D^{20} 1.348.

2. Reaction of Tetrafluoroethylene with Boron Trichloride under Pressure. A rotating stainless steel autoclave, of 0.5 liter volume, fitted with thermocouple socket, valve, and manometer, was rinsed with acid-free nitrogen and evacuated to a residual pressure of 2-3 mm. Into the autoclave were placed in turn 36 g of boron trichloride and 25 g of tetrafluoroethylene. The autoclave was rotated for 12-14 hours at 150° and 30-35 atm. At the conclusion of the reaction the contents of the autoclave were emptied through the valve into collecting vessels cooled respectively with carbon dioxide (-50°) and liquid air. After several distillations of the substance collected in the vessel cooled with carbon dioxide, besides unreacted boron trichloride, a fraction was isolated with b. pt. 70°, d_4^{20} 1.532, n_D^{20} 1.4360, namely, trichlorofluoroethylene.

Found %: C 16.62; F 12.90. C_2FCl_3. Calculated %: C 16.08; F 12.72.

The liquid, in amount 24.5 g, from the collector placed in liquid air, was distilled into sulfuric ether. After evaporation of the ethereal solution 4 g of the etherate of boron fluoride was isolated, with b. pt. 126°, d_{20}^{20} 1.120, n_D^{20} 1.347.

SUMMARY

It was shown that, as a result of reacting tetrafluoroethylene with boron trichloride, halogen exchange take place with formation of trichlorofluoroethylene and boron trifluoride.

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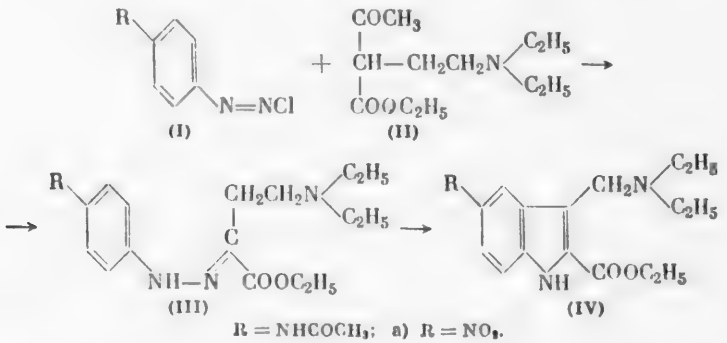
CYCLIZATION OF SUBSTITUTED PHENYLHYDRAZONES OF THE ETHYL ESTER OF α-KETO-γ-DIETHYLAMINOBUTYRIC ACID, USING THE METHOD OF E. FISCHER

A. Ya. Berlin and V. N. Zaitseva

Institute of Experimental and Clinical Oncology, Academy of Medical Sciences of the USSR

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2368-2371,
July, 1960
Original article submitted July 21, 1959

The purpose of this work was the synthesis of certain substituted indole derivatives. For this, cyclization by the method of E. Fischer was employed [1], starting from the p-acetamino- or the p-nitrophenylhydrazone of the ethyl ester of α-keto-γ-diethylaminobutyric acid (III and IIIa) according to the scheme.



R = NHCOCH₃; a) R = NO₂.

Condensation of salts of p-acetamino- and p-nitrophenyldiazonium (I and Ia) with the diethylaminoethylacetoacetic ester (II) [2] was achieved by the method worked out by V. V. Feofilaktov [3]. Conversion of phenylhydrazones (III and IIIa) into 2-carbethoxy-3-diethylaminomethyl-5-acetaminoindole (IV) and 2-carbethoxy-3-diethylaminomethyl-5-nitroindole (IVa) was carried out in the presence of polyphosphoric acid [4], which proved to be one of the best cyclization agents for use in the Fischer reaction [5].

It is known that the character of the substituent in the aromatic nucleus of the initial phenylhydrazone has a significant effect on ease of cyclization. The presence in the aromatic nucleus of a nucleophilic amino-group or a substituted amino-group usually facilitates cyclization [6], whereas introduction of electrophilic substituents such as nitro-groups, leads to inhibition of the reaction [6,7]. Indications occur [8] even of the complete failure of experiments on cyclization by the E. Fischer method of the o, m-, and p-nitrophenylhydrazones of the ethyl ester of pyrotartaric acid and many similar compounds. Nevertheless, in recent years a series of experiments has been successful in accomplishing cyclization of certain nitrophenylhydrazones of esters of α-ketoacids. For example Feofilaktov and Semenova [6] cyclized the p-nitrophenylhydrazone of the diethyl ester of α-ketoglutaric acid into the ethyl ester of 5-nitro-2-carbethoxy-3-indolylacetic acid; Cavallini and Ravenna [9] synthesized 2-carbethoxy-5-nitroindole from the p-nitrophenylhydrazone of the ethyl ester of pyrotartaric acid; starting from the latter compound and its ortho-and meta-isomers, Parmerter, Cook, and Dixon [10] by cyclization, saponification, and decarboxylation obtained 4-, 5-, 6-, and 7-nitroindoles.

The results of our experiments tallied with the above observations regarding the influence of substituents on ease of cyclization. In fact, on heating the p-acetaminophenylhydrazone of the ethyl ester of α-keto-γ-diethylaminobutyric acid (III) with polyphosphoric acid for 2 hours at 114-120°C, 68.3% of a derivative of 5-acetaminoindole (IV) was obtained, whereas, in the case of the p-nitrophenylhydrazone of the same acid (IIIa), heating at 120-140° for about the same period of time led to the formation in all of only 39.1% of the corresponding 5-nitroindole (IVa).

The following observation was of extreme interest. In an attempt to achieve cyclization of p-acetaminophenylhydrazone (III) by heating it with a 50% solution of H_2SO_4 in alcohol, p-phenylenediamine sulfate was unexpectedly obtained from the reaction mixture instead of the expected indole derivative. Formation of this compound under these reaction conditions indicates that, at least in this instance, we had for the first time come across an occasion where the free radical mechanism of the Fischer reaction had operated. Doubtless, the formation of p-phenylenediamine in this experiment had resulted from the fact that the rupture of the N-N bond in the initial phenylhydrazone (III) occurred earlier than the formation of the C-C bond in the ortho-position to the nitrogen atom. Hydrolysis of the acetamino-group had taken place simultaneously. This fact is of great significance from the point of view of understanding the mechanism of the E. Fischer reaction. The latter should not yet be considered as finally established even now [12], despite the fact that the problem has existed for over 75 years.

EXPERIMENTAL

β-Diethylaminoethylacetoacetic Ester (II). To the sodium acetoacetic ester (from 11.5 g of sodium in 380 ml of dry benzene and 66.5 g of freshly distilled acetoacetic ester) 67.8 g of diethylaminoethyl chloride was added dropwise at 50°C with stirring. The liquid was boiled under a reflux condenser for 4 hours and was poured into a mixture of 380 g of ice and 65 ml of conc. HCl. The aqueous layer was separated, and made alkaline with caustic soda solution until a weakly alkaline reaction was obtained with phenolphthalein. The reaction product separating out was isolated, and the aqueous layer extracted with ether. The ethereal solution was added to the main portion of the product, and dried with calcined potash. After distillation of solvent, 62.8 g (54.8%) of the ester was obtained; b. pt. 94-95° (2 mm), n_D^{21} 1.4460.

Found %: C 62.9, 62.8; H 9.97, 10.02; N 5.96, 6.28. $C_{12}H_{23}O_3N$. Calculated %: C 62.85; H 10.08; N 6.11.

Yellowing took place gradually on storage, even in the dark.

p-Acetaminophenylhydrazone of the Ethyl Ester of α-Keto-γ-diethylaminobutyric acid (III). From 20 g of finely ground p-aminoacetanilide, 80 ml of water, 220 g of ice and 64 ml of conc. HCl, by addition of a solution of 11 g of sodium nitrite in 100 ml of water, was obtained a diazo solution, to which, to remove excess HCl, was added on cooling 88.8 g of sodium acetate. To a mixture, cooled with ice, of 34 ml of 12% caustic soda solution and 144 g of crushed ice was simultaneously added dropwise with vigorous stirring the cold diazo solution and 30.56 g of diethylaminoethylacetoacetic ester. During this, the pH of the solution was not allowed to exceed 5.5-6, but, as acetic acid formation proceeded during the reaction, addition of alkali was necessary. In this case, 12.5 ml of a 12% caustic soda solution was added during the reaction. After mixing for 4 hours, the precipitate separating out was isolated, ground with 2N soda solution and extracted with chloroform. The chloroform solution was dried with calcined potash, the solvent distilled off, and the butyric residue ground to a yellow powder with petroleum ether. Yield, 31.91 g (68.8%). After recrystallization from a mixture of benzene and petroleum ether (3:2) the phenylhydrazone was obtained as bright-yellow crystals; m. pt. 112-113°.

Found %: C 61.94, 62.18; H 8.04, 8.15; N 15.96, 15.83. $C_{18}H_{28}O_3N_4$. Calculated %: C 62.10; H 8.10, N 16.08.

2-Carbethoxy-3-diethylaminomethyl-5-acetaminoindole (IV). A mixture of 0.4 g of p-acetaminophenyl hydrazone (III) and 10 g of polyphosphoric acid $H_5P_3O_{10}$ was heated with stirring for 2 hours at 114-120° (internal). On a subsequent day the dark, viscous product formed was poured into 100 ml of ice water, the solution neutralized with 12% NaOH to pH 8, and the product extracted with chloroform. After drying with calcined potash and distillation of solvent in vacuo, 0.26 g (68.3%) was obtained. The indole, recrystallized from benzene, took the form of bright-yellow, slender needles; m. pt. 140-141°.

Found %: C 64.99, 64.85; H 7.54; N 12.40, 12.25. $C_{18}H_{25}O_3N_3$. Calculated %: C 65.26; H 7.60; N 12.67.

Formation of p-Phenylenediamine from the p-Acetaminophenylhydrazone of the Ethyl Ester of α-Keto-γ-

diethylaminobutyric Acid. A mixture 0.58 g of the phenylhydrazone (III) and 6.65 ml of 50% sulfuric acid in absolute alcohol was boiled on a water bath for 4 hours. After about 1 hour, brilliant crystals began to separate out from the solution, and were then filtered off, washed with alcohol, and recrystallized from water; m. pt. 310° (decomposing).

Found %: C 34.84, 34.82; H 4.96, 4.85; N 12.59, 12.30. $C_6H_8N_2 \cdot H_2SO_4$. Calculated %: C 34.94, H 4.85, N 13.59.

p-Nitrophenylhydrazone of the Ethyl Ester of α-Keto-γ-diethylaminobutyric Acid (IIIa). A solution of 4.6 g of p-nitroaniline in 33 ml of dilute (1:1) hydrochloric acid was poured into 38 g of crushed ice, and to the mixture with vigorous stirring was immediately added a cooled solution of 2.53 g of sodium nitrite in 25 ml of water. Then to the diazo solution previously obtained was added 22 g of sodium acetate. To a mixture of 8.9 ml of 12% caustic soda and 36.5 g of crushed ice simultaneously was added with stirring the diazo solution and 7.64 g of diethylaminoethylacetoacetic ester (II). During the reaction the pH was kept within the limits 5.5-6 by addition of caustic. Under these conditions, 6.9 g of a dark, viscous substance was formed. To the reaction product was added 20 ml of anhydrous ethanol saturated with hydrogen chloride, and the mixture boiled under a reflux condenser for 1 hour. A bright-yellow crystalline precipitate of p-nitrophenylhydrazone hydrochloride (IIIa) then separated out. Yield, 4.44 g (35.8%); m. pt. 184-185° (from alcohol).

Found %: C 51.85, 51.59; H 6.99, 7.06; N 14.95, 15.20; Cl' 8.92, 9.24. $C_{16}H_{24}O_4N_4 \cdot HCl$. Calculated %: C 51.50; H 6.76; N 15.08; Cl' 9.51.

Preparation of the p-nitrophenylhydrazone base from the hydrochloride was not successful.

2-Carbethoxy-3-diethylaminomethyl-5-nitroindole (IVa). A mixture of 1.08 g of p-nitrophenylhydrazone hydrochloride and 11 g of polyphosphoric acid $H_5P_3O_{10}$ was heated for 2 hours at 120° and for 10 minutes at 140°. On a subsequent day the reaction product was poured into ice water, the precipitate filtered off, and the filtrate neutralized with 12% caustic soda to pH 8. The reaction product was extracted with chloroform, and the chloroform solution dried with calcined potash. After distillation of solvent, 0.36 g (39.1%) of the nitro-derivative of indole was obtained. A yellow substance with m.pt. 148.5–149.5° (from benzene).

Found %: C 60.10, 59.83; H 6.53, 6.61; N 13.05, 13.42. $C_{16}H_{21}O_4N_3$. Calculated %: C 60.19; H 6.63; N 13.16.

SUMMARY

1. By condensation of a diethylaminoethylacetoacetic ester with p-acetaminophenyldiazonium, the p-acetaminophenylhydrazone of the ethyl ester of α-keto-γ-diethylaminobutyric acid was obtained, and by cyclization was converted to 2-carbethoxy-3-diethylaminomethyl-5-acetaminoindole.

2. From a diethylaminoethylacetoacetic ester and p-nitrophenyldiazonium was prepared the p-nitrophenylhydrazone of the ethyl ester of α-keto-γ-diethylaminobutyric acid, which was converted into 2-carbethoxy-3-diethylaminomethyl-5-nitroindole.

3. By the action of 50% sulfuric acid in ethanol on the p-acetaminophenylhydrazone of the ethyl ester of α-keto-γ-diethylaminobutyric acid, p-phenylenediamine sulfate was formed.

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FLUORINATION OF A COMPLEX ACETONITRILE WITH BORON TRIFLUORIDE

M. A. Englin, S. P. Makarov, S. S. Dubov, L. A. Krasnousov, and A. Ya. Yakubovich

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2371-2374, July, 1960
Original article submitted July 1, 1959

By fluorination of acetonitrile vapor over copper, Bigelow [1] obtained $CF_2=NF$ and $CHF_2CF=NF$. Somewhat later, Cuculo and Bigelow [2] described the reaction of acetonitrile vapor and elementary fluorine over a copper grid, $CF_3CF_2NF_2$, $CF_2=NF$, CF_4, and ethane fluoroderivatives being formed. By fluorination of acetonitrile over gold, Haszeldine [3] obtained perfluoroethylamine. The communications of Nerdel [4] and Hückel [5] describe the reaction of acetonitrile and mercuric fluoride at 150-180°C, where $CH_3CF=NF$, $CH_2=CFNF_2$, $CH_3CF_2NF_2$, and $CH_2=C-NF$ are obtained. However, the authors cited do not quote constants for these compounds nor proof of their structure.

In the present communication is described the fluorination by diluted fluorine of an acetonitrile complex with boron trifluoride in a copper reactor at room temperature.

By fractional distillation of the fluorination products were obtained NF_3, CH_3CF_3, CHF_2CN, and two new substances: one with b. pt. −25 to −24.5° and the other with b. pt. −4.8 to −4.7° together with a considerable quantity of unchanged acetonitrile.

The substance with b. pt. −25 to −24.5° is a colorless gas of molecular weight 97.5. This gas is completely decomposed by alcoholic potash, does not liberate iodine from an alcoholic solution of KI, does not combine with bromine, decolorizes an aqueous-alkaline solution of potassium permanganate, dissolves in organic solvents and to a limited extent in water. Its composition by elements and its molecular weight indicate the molecular formula $C_2H_2NF_3$. The structure of such a compound, considering it is formed on fluorination of acetonitrile, must be represented by the following very probable isomers.

$CH_2=CFNF_2$ (I) $CH_2FCF=NF$ (II) CH_2-CF_2 with NF bridge (III)

To clarify the structure of the substance described, its IR-spectrum was observed, in which were found the following bands, where v.i. means very intense, i. intense, m.i. medium intensity, w.i. weak intensity:

840 (i.), 883 (m.i.), 976 (v.i.), 1064 (v.i.), 1102 (v.i.), 1180 (v.i.), 1190 (v.i.), 1300 (v.i.), 1370 (i.), 1422 (i.), 1458 (i.), 1472 (i.), 1620 (w.i.), 2990 (i.) cm^{-1}.

The band at 2990 cm^{-1} is characteristic of C-H-bonds, the group of bands in the region 1000-1400 cm^{-1} is caused by vibrations of C-F. Evidently, the intense band at 976 cm^{-1} must be attributed to the valence vibration of the N-F-bond. As all three conjectured structural formulas of the substance $C_2H_2NF_3$ are characterized by the presence of the bonds C-H, N-F, and C-F, the portion of the spectrum establishing its structure must be that in the region of the frequencies corresponding to the double bonds C=C and C=N. From the literature it is known

that for fluorinated unsaturated compounds the absorption bands characteristic for C=C and C=N bonds differ greatly in intensity and are within the limits 1650-1872 cm^{-1} [6], which, however, in this instance were not detected.

Thus, the formula of structures (I) and (II) of the substance $C_2H_2NF_3$ are not confirmed by the spectroscopic data, and so formula (III) is more likely. Confirming a cyclic structure of this compound is done by the presence in the IR-spectrum of absorption bands at 840 and 883 cm^{-1}, which must be interpreted as deformation vibrations of a three-membered ring, this agreeing with the similar data of Thompson and Cave [7], after having investigated the vibration spectra of ethyleneimine.

Hence, according to its chemical properties, molecular weight, and characteristic IR-spectrum frequencies, to the substance investigated must be attributed the formula of fluorinated ethyleneimine.

The substance with b. pt. −4.8 to −4.7°, in the gaseous and liquid states is colorless, has a molecular weight 117, does not liberate iodine from an alcoholic solution of KI, does not decolorize an aqueous-alkaline $KMnO_4$ solution, and dissolves in alcohol and benzene. Its constitution by elements and molecular weight corresponds to the molecular formula $C_2H_3NF_4$. A substance of such a composition must have several isomeric structures. In fluorination of acetonitrile the formation of the isomer $CH_3CF_2NF_2$ is the most likely.

In the IR-spectrum of the substance there are absorption bands at 940 and 3000 cm^{-1}, which must correspond respectively to N-F and C-H bonds, and there is also a group of bands in the region 1000-1400 cm^{-1} caused by C-F vibrations. An absorption band in the region of double bonds is not observed. All these properties agree well with the structure proposed above for this substance, that of α, α,N,N-tetrafluoroethylamine.

On fluorination of the complex $CH_3CN \cdot BF_3$ by elementary fluorine, a considerable amount (about 36%) of acetonitrile remains unchanged and on removal from the sphere of reaction collects in the receiver together with the fluorination products. Yields of fluorination products, calculated from the acetonitrile used, are equal to: NF_3 6.5%, CH_3CF_3 5%, CH_2CF_2NF 3%, $CH_3CF_2NF_2$ 2.5%, and CHF_2CN 1%.

From the structure of the substances obtained it follows that on fluorination of acetonitrile mainly C≡N bonds enter into the reaction, and also that substitution of hydrogen atoms by fluorine takes place in the methyl group. Predominant fluorination at the C≡N-bond is in accord with the energies of the bonds C–H (87.3 kcal / mole) and C–N (48.6 kcal /mole) [8].

The fluorination must be represented by the following scheme.

$$CH_3C{\equiv}N \xrightarrow{F_2} [CH_3CF{=}NF] \xrightarrow{F_2} CH_3CF_2NF_2$$

$$CH_3CF_2NF_2 \xrightarrow{F_2} CH_3CF_3 + NF_3$$

$$CH_3CN \xrightarrow{F_2} [CH_2FCN] \xrightarrow{F_2} CHF_2CN$$

The path that trifluoroethyleneimine formation follows is not quite clear. It must be assumed that its formation occurs as a result of conversion of free radicals formed during the fluorination process.

EXPERIMENTAL

The complex $CH_3CN \cdot BF_3$ was prepared by passing BF_3 into acetonitrile at room temperature [9].

Fluorination of the complex $CH_3CN \cdot BF_3$. Into a copper reactor (diameter 25 mm, height 250 mm) was introduced 40 g of complex mixed with 40 g of calcined KF and 40 g of small cylinders (diameter 3-5 mm, height 10-15 mm) prepared from a brass mesh. Fluorine, diluted to 10-20% with nitrogen, was passed into the lower part of the reactor at room temperature at a flow rate of 6-10 liters/hour. The fluorination products were purified with a mixture of calcined KF and NaF (with HF as a binder) and condensed in receivers cooled to -80° and -190°. After 6 hours of fluorination, 3.5 g of products was obtained boiling at -80°, and 5.6 g of a liquid which did not boil at room temperature. From the receiver cooled with liquid air, after vaporization and washing the gas with baryta water (to remove CO_2 and BF_3) 1.8 liters of gas was obtained. After fractional distillation had been carried out three times on 75 g of the carbonate condensate, three pure substances separated on the low-temperature column: with b.pt. -47.5-46°, 11 g (1st fraction), with b. pt. -25-24.5°, 8 g (2nd fraction), and with b. pt. -4.8-4.7°, 8 g (3rd fraction).

1st fraction.

Found %: C 28.47, 27.50; H 5.48, 5.77; F 66.06, 66.96. M 86.0, 85.5. $C_2H_3F_3$. Calculated %: C 28.6; H 3.58; F 67.8. M 84.

From analysis, molecular weight, and boiling point, the substance was 1,1,1-trifluoroethane (b. pt. -46.7° [10]).

2nd fraction. Colorless in the liquid and gaseous states.

Found %: C 21.7; H 1.3; N 14.28, 15.40; F 58.86, 59.39. M 96.5, 97.5. $C_2H_3NF_2$. Calculated %: C 24.7; H 2.06; N 14.35; F 58.8. M 97.0.

The IR-spectra of the 2nd and 3rd fractions were taken on a "Perkin Elmer" spectrometer, model 12-B, with automatic recording in the region 800-4000 cm^{-1} in the gaseous state in a cell 120 mm long with sylvite openings under a pressure in the cell from 700 to 5 mm.

3rd fraction exploded on heating above 200°.

Found %: N 13.7, 13.5; F 66.06, 66.96, M 115, 119. $C_2H_3NF_4$. Calculated %: 11.95; F 65.0 M 117.

On fluorination of 1 kg of the complex $CH_3CN \cdot BF_3$ a 150 g yield was obtained, boiling above 20°, from which was withdrawn 4 g of a fraction boiling at 14-18° (containing C,H,N,F), not examined more closely, and 2 g of a fraction with b. pt. 22-24°. All of the residue distilled at 80-82° and proved to be unchanged acetonitrile, containing on analysis a small quantity of fluorine (apparently in the form CH_2FCN).

Fraction 22-24°.

Found %: C 28.87, 30.14; H 2.28, 3.4; F 48.5. C_2HNF_2. Calculated %: C 31.2; H 1.37; F 49.4.

From analysis and boiling point this was CHF_2CN (b. pt. 22.8-23.4°) [11].

After treatment with baryta water of 10 liters of fluorination products of the complex $CH_3CN \cdot BF_3$, boiling below -80°, 11 g of a colorless liquid (in liquid air) was obtained, mixed with white crystals. After separation from the crystals and distillation, 3.2 g of NF_3 was isolated, with b. pt. -122-120°, M 75 (according to the data in the literature [12]: b. pt. —129°).

SUMMARY

On fluorination of a complex of acetonitrile with boron trifluoride by means of elementary fluorine, nitrogen trifluoride, 1,1,1-trifluoroethane, difluoroacetonitrile, and N-fluoro-α,α-difluoroethylamine ($CH_3CF_2NF_2$), not described in the literature, and N-fluoro-1,1-difluoroethyleneimine ($\underline{CH_2\ CF_2NF}$) were obtained. The scheme for the formation of the fluorination products was discussed.

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FLUORINATION OF SILVER AND POTASSIUM CYANATES

A. Ya. Yakubovich, M. A. Englin, and S. P. Makarov

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2374-2377, July, 1960
Original article submitted July 1, 1959

By fluorinating silver cyanide, Ruff and Giese [1] obtained a large number of different polyfluorinated compounds and a characteristic of this process was the formation of fluoro derivatives with a larger number of carbon and nitrogen atoms than in the original silver cyanide. Thus, together with the simplest fluoro derivatives (CF_4, CF_3NO, COF_2, SiF_4, C_2F_6), the authors isolated considerable amounts of $(CNF_3)_2$, $(CNF_3)_3$ and $(CNF_4)_2$.

In the present work, we describe the analogous (heterogeneous) fluorination of silver and potassium cyanates. The reaction was carried out by treating a mixture of the starting cyanate and calcium fluoride with elementary fluorine diluted with nitrogen at 25-55°. The fluorination rate was insignificant at lower temperatures.

The fluorination of silver cyanate formed carbonyl fluoride, COF_2 (72%) and carbon dioxide (24.5%). No other nitrogen-containing substances could be detected in the reaction products. The latter is evidently explained by the fact that the nitrogen from the cyanate was converted into the elementary state and it was difficult to establish its presence as the starting fluorine was strongly diluted with nitrogen. The silver cyanate was quantitatively converted to silver difluoride.

Fluorination of potassium cyanate yielded trifluoromethyl hypofluorite, CF_3OF (about 80%) and nitrogen trifluoride, NF_3 (about 60%) together with potassium fluoride and small amounts of carbon dioxide and carbonyl fluoride.

Trifluoromethyl hypofluorite was synthesized previously by fluorination of carbon monoxide [2] or methanol vapor [3] at 160-180° on a silvered copper catalyst. The high yield of trifluoromethyl hypofluorite from the fluorination of potassium cyanate makes it possible to recommend this method for preparative purposes [4]. The formation of appreciable amounts of carbon dioxide in the reaction product is evidently explained by the oxidizing action of oxygen, catalyzed by elementary fluorine [5], which was present in the fluorine we used in up to 7% by volume.

From what has been presented it follows that the fluorination of cyanates is considerably affected by the nature of the salt-forming metal. The halogenation of carboxylates, where the metal is connected to oxygen as in cyanates, is known to form acyl hypohalites RCOOX, which are stable in solution [6]. Analogously, the fluorination of fluorine-substituted carboxylic acids yields stable acyl hypofluorites [7].

It may be assumed that in the case of cyanates, fluorination begins with the formation of the corresponding hypofluorite FOCN. However, we were unable to detect this compound in the fluorination products and this may be explained by its great tendency for further fluorination at the C≡N bonds according to the scheme:

$$MeOC{\equiv}N \xrightarrow{F_2} [FOC{\equiv}N] \xrightarrow{F_2} [FOCF_2NF_2] \xrightarrow{F_2} FOCF_3 + NF_3$$

However, the scheme examined, which agrees well with the results of fluorination of potassium cyanate, does not reflect all the processes occurring during the action of fluorine on silver cyanate. This indicates that the fluorination of the cyanates proceeds evidently according to different schemes.

With acetonitrile, Bigelow et al. [8] showed that the action of elementary fluorine on this compound results in not only substitution, but also the addition of fluorine at the C ≡ N triple bond. We found that in the heterogeneous fluorination of the complex $CH_3CN \cdot BF_3$, the addition of fluorine at the C ≡ N bond is the predominating reaction and results in the formation of $CH_3CF_2NF_2$ [9].

On this basis, it may be considered that the fluorination of cyanates begins not with replacement of the metal by fluorine, but with addition of the latter at the C ≡ N triple bond according to the scheme:

$$MeOC{\equiv}N \xrightarrow{F_2} [MeOCF_2NF_2] \xrightarrow{F_2} [MeOCF_3] + [NF_2].$$

As a result of further conversion of the intermediate metal trifluoromethylate (depending on the nature of the metal), either carbonyl fluoride or trifluoromethyl hypofluorite may be formed.

$$[NF_2 + MeOCF_3] \xrightarrow{F_2} \begin{cases} \xrightarrow{Me=Ag} AgF_2 + COF_2 + N_2 \\ \xrightarrow{Me=K} KF + CF_3OF + NF_3 \end{cases}$$

The fact that the formation of trifluoromethyl hypofluorite proceeds according to the scheme examined and not as a result of subsequent fluorination of carbonyl fluoride is indicated on the one hand by the ease of formation of this compound during fluorination of potassium cyanate (50-55° instead of 160-180°, which is required for the conversion of COF_2 into CF_3OF on silver) and on the other hand by the fact that in the fluorination of silver cyanate, i.e., in the presence of AgF_2 formed (which is a fluorination catalyst), the reaction stops at carbonyl fluoride.

EXPERIMENTAL

A copper reactor (25 mm in diameter and 250 mm in height) was charged with a mixture of equal weights of silver or potassium cyanates and dry potassium fluoride in cylinders (3-6 mm in diameter and 10-15 mm in height) of brass gauze. The fluorine-nitrogen mixture containing 5-8% of fluorine was introduced into the bottom of the reactor at 7-13 liter/hr. The AgOCN was fluorinated 25-30° and the KOCN at 50-55°. The fluorination products were freed from HF with a mixture of baked potassium and sodium fluorides and collected in a trap cooled with liquid air.

Fluorination of silver cyanate. We fluorinated 15 g of 91% salt. Distillation of the reaction products yielded 5.3 g of a fraction with b.p. -85-83°. The product reacted with aniline to form diphenylurea with m.p. 235-236° (from methanol). A mixed melting point was not depressed.

Found %: N 13.65. $C_{13}H_{12}ON_2$. Calculated %: N 13.2.

According to the fluorine content (46.8-47.0%) and molecular weight (59.0 and 59.2), the fraction with b.p. -85-83° was a mixture of 81.5% COF_2 (b.p. -83.1° [10]) and 18.5% CO_2 (sublimation p. -78.2 [11]). After the fluorination, there remained in the reactor a white powder which contained AgF_2 in an amount equivalent to the silver content of the cyanate.

Fluorination of potassium cyanate. We fluorinated 16.5 g of salt. The reaction products (27 g), which condensed at liquid air temperature, were separated from the solid particles (COF_2 and CO_2) by siphoning and distilled on a low-temperature column. The first fraction had b.p. −127-125°, 8.5 g, and the second fraction had b.p. -95--93°, 16.5 g.

The first fraction was a colorless liquid at liquid air temperature. According to the molecular weight (70.2 and 70.4, calc. 71.0) and the boiling point (-129 [12]), the fraction was NF_3.

The second fraction remained liquid at liquid air temperature; it liberated iodine from KI solution.

Found %: C 11.3, 12.05; F 71.1; 72.1. F (active) 35.8, 35.9. M 101.4, 104.2. COF_4. Calculated %: C 11.54; F 73.1; F (active) 36.5. M 104.0.

According to molecular weight, elementary composition, the boiling point of -94.2±0.5° [3], and properties the fraction was CF_3OF. After fluorination, the reactor was found to contain KF in an amount equivalent to the amount of potassium in the cyanate.

SUMMARY

1. The only organofluorine product from the fluorination of silver cyanate by elementary fluorine was carbonyl fluoride.

2. Fluorination of potassium cyanate readily yielded trifluoromethyl hypofluorite (in about 80% yield) and nitrogen trifluoride.

3. A scheme for the formation of products from the fluorination of silver and potassium cyanates is discussed.

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SYNTHESIS OF SOME 2-HYDROXY-4-ALKOXYBENZOPHENONES

N. A. Larin, E. N. Matveeva, and V. S. Smirnova

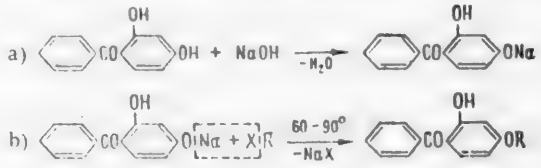
Scientific Research Institute of Polymerized Plastics

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2377-2379,
July, 1960
Original article submitted July 6, 1959

The literature contains descriptions of various hydroxymethoxybenzophenones, 4-hydroxy-4'-ethoxy-4,4'-diethoxy- [1], 4,4'-dipropoxy- [2], and 2,2'-diethoxybenzophenones [3], etc. 2-Hydroxy-4-methoxybenzophenone, which was prepared by methylation of the monosodium or potassium salt of 2,4-dihydroxybenzophenone [4], is known to be a good light stabilizer for a whole series of polymers [5].

In a search for good light stabilizers for polyethylene, we synthesized 2-hydroxy-4-ethoxy-, 2-hydroxy-4-n-propoxy, and 2-hydroxy-4-n-butoxybenzophenones. In addition, we obtained the condensation products of normal hexyl, octyl, nonyl, and decyl bromides with the monosodium salt of 2,4-dihydroxybenzophenone.

The 2-hydroxy-4-alkoxybenzophenones were obtained according to the following scheme:



The starting 2,4 dihydroxybenzophenone was obtained by Balyer's method [6] by fusion of benzoic acid with resorcinol in the presence of zinc chloride at 160-165°.

It should be noted that the alkoxylation of 2,4-dihydroxybenzophenone occurred only in position 4. This is indicated by the fact that methylation of the monosodium salt of 2,4-dihydroxybenzophenone with methyl iodide or dimethyl sulfate gave only 2-hydroxy-4-methoxybenzophenone, a crystalline substance melting at 62, 64, and 66° (data of different authors [7]), depending on the degree of purity, while the isomeric 4-hydroxy-2-methoxybenzophenone, which was obtained by another scheme, melts at 124° [8].

EXPERIMENTAL

1. 2-Hydroxy-4-ethoxybenzophenone. A solution of 2 g of dry sodium hydroxide in 5 ml of water was diluted with 15 ml of rectified alcohol and 10.7 g (0.05 mole) of 2,4-dihydroxybenzophenone was dissolved in the resultant solution at room temperature with vigorous shaking. Ethyl bromide* (4.2 ml) was then added with stirring. The flask was shaken vigorously for 1-2 min, connected to a reflux condenser, and placed on a water bath. The mixture was heated at 30-40° for 1 hr and then at 65-75° for 16 hr. The cooled mixture was treated with approximately 40 ml of water and extracted with ether (250 ml). The ether solution was washed with water and dried. After removal of the ether, the residue was recrystallized twice. We obtained 4.3 g (35%) of yellow-orange crystals with m.p. 54.5° (from 70% alcohol). The substance was difficultly soluble in water, but soluble in hot alcohol and benzene.

*Alkyl bromides and iodides were usually used; alkoxylation proceeded very slowly with alkyl chlorides.

Found %: C 74.02, 74.22; H 5.66, 5.74; OH 6.91, 7.02; OC_2H_5 [illegible]. M [illegible]. $C_{15}H_{14}O_3$. Calculated %: C 74.34; H 5.82; OH 7.02; OC_2H_5 18.59. M 242.1.

2. 2-Hydroxy-4-n-propoxybenzophenone. 2,4-Dihydroxybenzophenone (10.7 g) was dissolved in an aqueous alcohol solution of alkali (2 g NaOH + 4 ml H_2O + 18 ml alcohol). Propyl bromide (10 ml), approximately two-fold excess, was then added. The reaction mixture was shaken vigorously and heated under reflux on a water bath at 70-80° for 13 hr. When the flask was cooled, a dark orange precipitate formed and this was sucked dry on a Buchner funnel and treated with ether. The ether solution was washed with water and dried, the ether removed and the residue recrystallized. We obtained ~ 3.65 g (30%) of white crystals with a yellow tint with m.p. 67° (from 65% alcohol). The substance was difficultly soluble in water, soluble in hot alcohol and readily soluble in ether and benzene.

Found %: C 74.64, 75.04; H 6.16, 6.18; OH 6.91, 7.08; OC_3H_7 22.4, 22.5. M 247.6. $C_{16}H_{16}O_3$. Calculated %: C 74.96; H 6.29; OH 6.64; OC_3H_7 23.04. M 256.1.

3. 2-Hydroxy-4-n-butoxybenzophenone was obtained analogously in a yield of 5.4 g (about 40%); it formed greyish white crystals with m.p. 56-57° (from 80% alcohol). It was difficultly soluble in water, soluble in hot alcohol and readily soluble in ether and benzene.

Found %: C 75.4, 75.45; H 6.74, 6.65; OH 5.87, 6.14; OC_4H_9 26.8. M 265.7. $C_{17}H_{18}O_3$. Calculated %: C 75.52; H 6.7; OH 6.29; OC_4H_9 27.01. M 270.1.

Analogously, prolonged heating (18-23 hr) on a water bath* yielded the condensation products of the monosodium salt of 2,4-dihydroxybenzophenone with normal hexyl, octyl, nonyl, and decyl bromides. The identification of these condensation products is not yet complete.

Condensation product of Na salt of 2,4-dihydroxybenzophenone (%) with:	Melting point	Found (%)			Empirical formula	Calc. for corresp. 2-hydroxy-4-alkoxybenzophenone (%)			Yield (%)
		C	H	OH		C	H	OH	
n-$C_6H_{13}Br$	55.5°	76.7	7.33	5.49, 5.29	$C_{19}H_{22}O_3$	76.49	7.44	5.7	15
n-$C_8H_{17}Br$	45—46	76.88	7.8	5.6, 5.56	$C_{21}H_{26}O_3$	77.25	8.03	5.21	13—15
n-$C_9H_{19}Br$	50.5	77.5	8.2	—	$C_{22}H_{28}O_3$	77.6	8.26	—	28—30
n-$C_{10}H_{21}Br$	50	77.7	8.46	—	$C_{23}H_{30}O_3$	77.91	8.54	—	18

SUMMARY

1. The possibility of alkoxylation of 2,4-dihydroxybenzophenone in position 4 was demonstrated.

2. Alkoxylation of 2,4-dihydroxybenzophenone yielded 2 hydroxy-4-ethoxy-, 2 hydroxy-4-n-propoxy-, and 2-hydroxy-4-n-butoxybenzophenones and also the products from the condensation of an alkaline solution of 2,4-dihydroxybenzophenone with normal hexyl, octyl, nonyl, and decyl bromides.

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* The condensation with decyl bromide was carried out on a glycerol bath at 110-115° for 15 hr.

SULFONATION OF β-DIKETONES

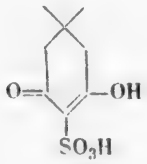
XI. DERIVATIVES OF DIMEDONE-2 SULFONIC ACID

É. Gudrinietse, G. Vanag, and L. Mazkal'ke

Riga Polytechnic Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2379-2387, July, 1960
Original article submitted July 9, 1959

2-Nitrodimedone is readily halogenated and forms 2-halo-2-nitrodimedones, in which the halogen is extremely labile [1,2]. Bromination of dimedonesulfonic acid (I) with bromine water forms 2-bromodimedone. Depending on the amount of bromine used, sodium dimedonesulfonate reacts with bromine in glacial acetic acid to give both 2-bromo- and 2,2-dibromodimedone. In this reaction, dimedonesulfonic acid behaves analogously to aromatic hydroxysulfonic acids [3].

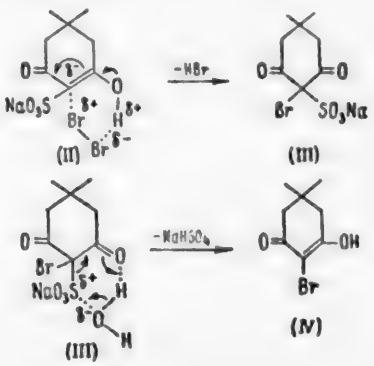


(I)

It has long been known that a sulfonic acid group at a carbon atom with a double bond is readily eliminated [4] and this has been confirmed with sulfonic acids of unsaturated aldehydes [5].

In our case, the ready elimination of the sulfonic acid group is evidently connected with the electromeric effect of the hydroxyl and keto groups.

During the attack of the electrophilic agent, namely, bromine, the active complex (II) may be formed and this may immediately yield 2-bromodimedonesulfonic acid (III). In compound (III) the C-S bond is strongly polarized and therefore is readily cleaved hydrolytically with the formation of 2-bromodimedone (IV), which is further brominated when excess bromine is present and forms 2,2-dibromodimedone.



Dimedonesulfonic acid reacts with other electrophilic agents (iodine chloride, sulfuryl chloride, nitric acid, and aryl diazo compounds) similarly to bromine and loses the sulfonic acid group.

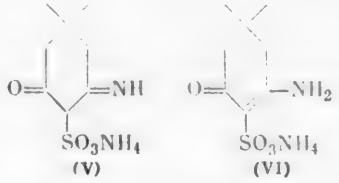
The reaction of sodium dimedonesulfonate in glacial acetic acid with the dioxane complex of iodine chloride ($C_4H_8O_2 \cdot 2ICl$) yielded 2,2-diiododimedone, which has not been described in the literature.

Sulfuryl chloride gives an almost quantitative yield of 2,2-dichlorodimedone with dimedonesulfonic acid.

Nitration of sodium dimedonesulfonate with fuming nitric acid in anhydrous ether yielded 2-nitrodimedone. In contrast to ω-acetophenonesulfonic acid, 2-arylhydrazonodimedones were formed in coupling reactions with aryl diazo compounds in neutral and alkaline media.

In all these cases of reactions with electrophilic reagents, for example nitration [7-10], chlorination [11], and iodination [12], dimedonesulfonic acid is similar to aromatic o-hydroxysulfonic acids.

Like sodium 1,3-indandione-2-sulfonate [13], when heated with ammonium acetate and glacial acetic acid, sodium dimedonesulfonate forms the imine of ammonium dimedonesulfonate, which may exist in two tautomeric forms (V, VI).



To establish the structure of the imine obtained, we plotted its infrared absorption spectra. Figure 1 shows that the vibrations of an unconjugated keto group (1700-1740 cm^{-1}) were absent. The absorption maxima at 1510 and 1655 cm^{-1} are largely characteristic of a conjugated enamine form. The valence vibrations of the S=O bond appeared at 1037 cm^{-1}. For comparison, we plotted the infrared spectrum of dimedone imine (Fig. 2).

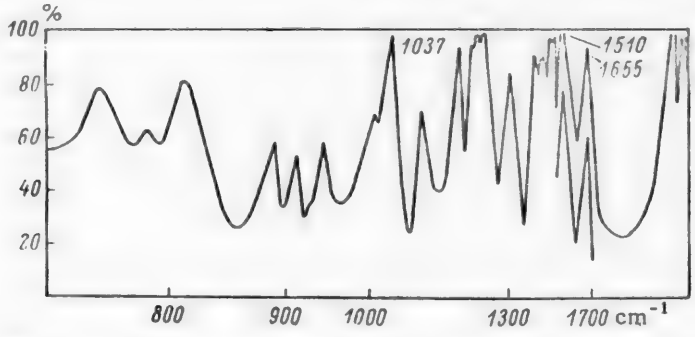
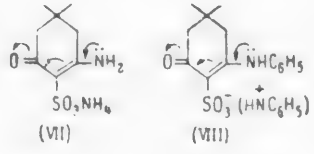


Fig. 1. Infrared spectrum of the imine of ammonium dimedone-2-sulfonate.

From the spectroscopic investigations it follows that the imine of ammonium dimedone-2-sulfonate exists in the enamine form (VI) and is an aminovinyl ketone, for which the mesomeric structure (VII) is more probable.



The phenylimine of aniline dimedone-2-sulfonate was obtained analogously. Since the spectrum of the phenylimine (Fig. 3) shows no characteristic absorption of an unconjugated carbonyl group and the absorption maximum at 1635 cm^{-1} may be assigned to the vibrations of a conjugated C=O bond, we consider that the phenylimine exists in the enamine form (VIII).

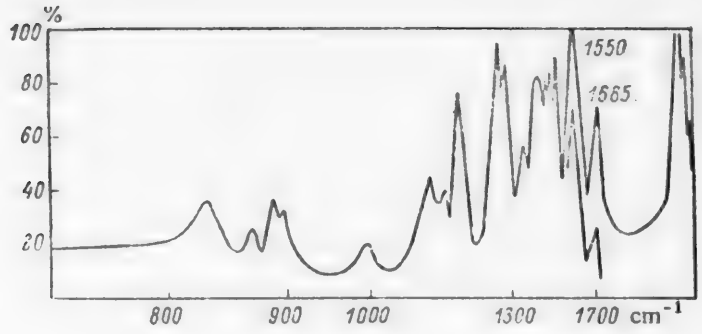


Fig. 2. Infrared spectrum of dimedone imine.

Derivatives of dimedonesulfonic acid substituted in the sulfonic acid group are obtained with difficulty. The chloride could not be obtained by the action of a three-fold excess of phosphorus pentachloride on sodium dimedonesulfonate. Chlorine-containing products were formed and these may have been analogous to those obtained from dimedone and phosphorus pentachloride [14]; they were not investigated in more detail.

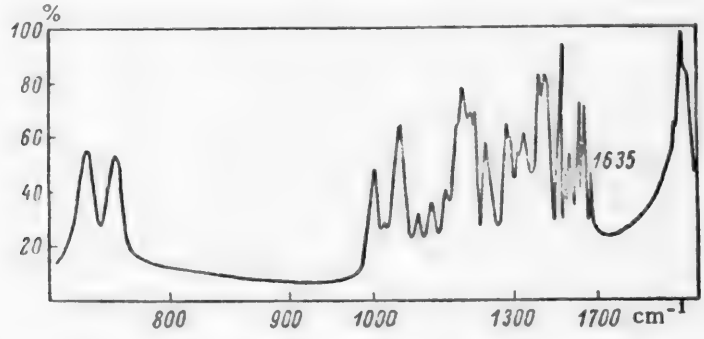
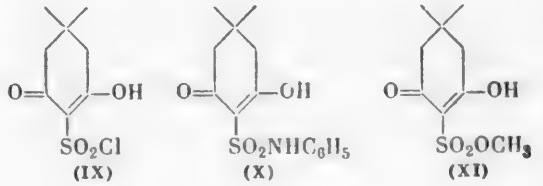


Fig. 3. Infrared spectrum of the phenylimine of aniline dimedone-2-sulfonate.

When equimolecular amounts of sodium dimedonesulfonate and phosphorus pentachloride were used, it was possible to obtain the sulfonyl chloride (IX); the latter was then converted into the anilide (X).



Dimedonesulfonyl chloride (IX) was also obtained by prolonged boiling of the sulfonic acid (I) with thionyl chloride. A partial reaction occurred, as by the action of aniline on the reaction mixture it was possible to isolate the aniline salt of dimedonesulfonic acid in addition to the anilide (X).

An attempt to prepare the sulfonyl chloride from sodium dimedone-2-sulfonate and chlorosulfonic acid [15-17] did not give positive results.

The structure of the anilide (VIII) was confirmed by the infrared absorption spectrum (Fig. 4), in which the frequency 1154 cm^{-1} (1165-1135 cm^{-1} [18]) corresponded to the symmetrical valence vibrations of the S=O bond, and the frequencies of 1592.5 and 1643 cm^{-1}, to the C=C and C=O conjugated bonds.

We obtained methyl dimedone-2-sulfonate by the action of diazomethane on dimedonesulfonic acid [19, 20]. Methyl dimedone-2-sulfonate (XI) dissolved in water readily with an acid reaction. In a benzene solution

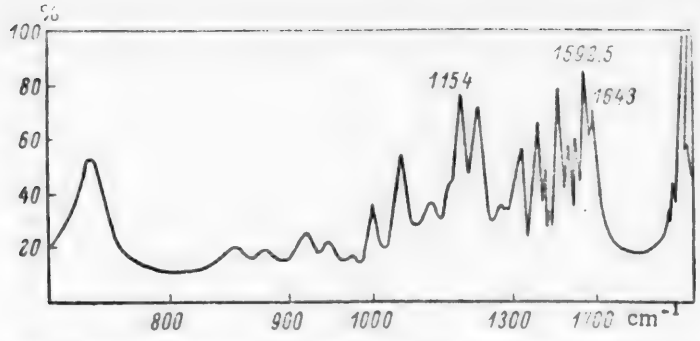


Fig. 4. Infrared spectrum of the anilide of dimedone 2-sulfonic acid.

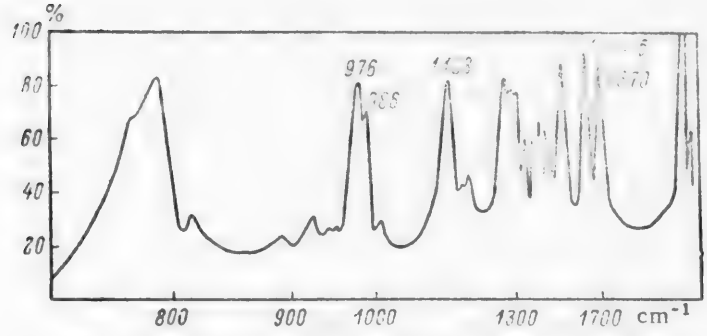
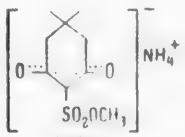
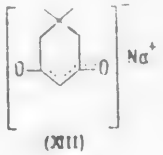


Fig. 5. Infrared spectrum of methyl dimedone-2-sulfonate.

with ammonia, it formed the ammonium salt of methyl dimedone-2-sulfonate (XII).



(XII)



(XIII)

The fact that methylation occurred at the sulfonic acid group [21] and not at the enol hydroxyl group [22] is indicated by the displacement of the absorption band of the S = O bond toward higher frequencies in the spectra of the ester (Fig. 5) and its ammonium salt (Fig. 6) in comparison with the spectra of the sulfonic acid salts.

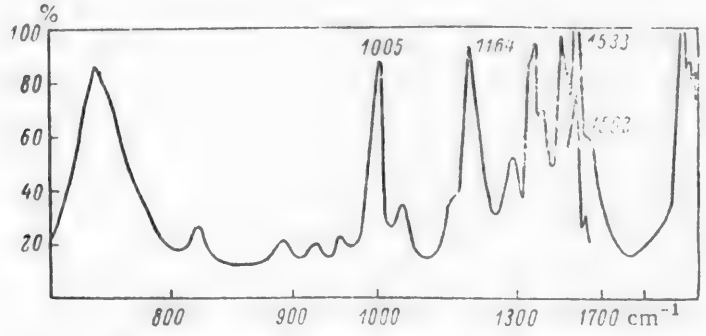


Fig. 6. Infrared spectrum of the ammonium salt of methyl dimedone-2-sulfonate.

In the literature [23] it is reported that the symmetrical valence vibrations of S=O in covalent sulfonates give frequencies in the range 1200-1145 cm^{-1} and for sulfonic acid salts, 1060-1030 cm^{-1}, while methyl dimedone-2-sulfonate absorbed at 1128 and its ammonium salt at 1164 cm^{-1}. As yet, it is difficult to explain why the frequency of the S=O valence vibrations of the ester itself (1128 cm^{-1}), though considerably higher than for dimedonesulfonic acid salts, are still lower than for the ammonium salt of the methyl ester (1164 cm^{-1}) and lie below the limit reported in the literature.

The structure of compounds (XI) and (XII) were confirmed by the absorption characteristic of the dimedone anion which was observed in the spectrum of the ammonium salt of the methyl ester, namely, one intense maximum at 1533 and a second small maximum at 1592.5 cm^{-1} (only an inflection point appears at high concentrations). For comparison, we plotted the infrared absorption spectrum of the sodium salt of dimedone (Fig. 7) (XIII).

The frequency of 1005 cm^{-1} in the spectrum of the ammonium salt of the methyl dimedone-2-sulfonate and the frequency of 976-986 cm^{-1} in the spectrum of methyl dimedone-2-sulfonate correspond to the vibrations of the methoxyl group.

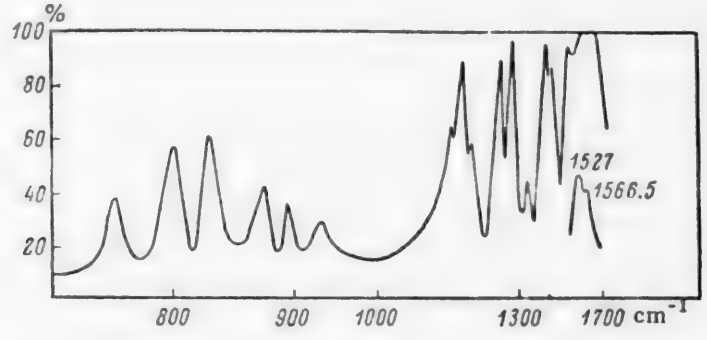


Fig. 7. Infrared spectrum of the sodium salt of dimedone.

EXPERIMENTAL

Nitration of sodium dimedone-2-sulfonate. With stirring, 2.6 ml of fuming nitric acid was added to 4.82 g sodium dimedone-2-sulfonate and 25 ml of anhydrous ether in a three-necked flask with a stirrer, thermometer, and dropping funnel. The solution acquired a dark red color, which rapidly changed to yellow. After the mixture had been stirred for 3 hr, the ether was removed by suction and a few drops of water were added to the residue. The 2-nitrodimedone was washed on the filter with a small amount of water. We obtained 2.37 g (62%) of 2-nitrodimedone. The m.p. was 102° (102-103° [1, 24]).

Reaction of sodium dimedone-2-sulfonate with sulfuryl chloride. With water cooling, 2.42 g of well ground sodium dimedone-2-sulfonate was added to 6 ml of sulfuryl chloride. The homogeneous solution was poured onto ice. The product was recrystallized from ethanol. We obtained 1.7 g (80%) of 2,2-dichlorodimedone crystals. The m.p. was 111° (112° [25]).

Bromination of sodium dimedone-2-sulfonate. After 20 min, a solution of 2.42 g of sodium dimedone-2-sulfonate and 1.6 g of bromine in 30 ml of glacial acetic acid deposited 1.1 g (50%) of 2-bromodimedone crystals. The product was recrystallized from benzene. The m.p. was 174-175° (175° [25]). The product did not depress the melting point of 2-bromodimedone obtained by direct bromination of dimedone. 2-Bromodimedone was also obtained by the addition of bromine water to an aqueous solution of sodium dimedone-2-sulfonate until it was completely decolorized. Bromination with a molar ratio of dimedone to bromine of 1:3 for 2 hr yielded 2,2-dibromodimedone (79%). After recrystallization from carbon tetrachloride, the product had m.p. 143-144° (144° [25]). The product did not depress the melting point of 2,2-dibromodimedone obtained by the method in [25].

Reaction of sodium dimedone-2-sulfonate with dioxane complex of iodine chloride [2]. A few minutes after 2.05 g of the dioxane complex of iodine chloride had been added to a solution of 2.42 g of sodium dimedone-2-sulfonate in 20 ml of glacial acetic acid, a homogeneous, red-brown solution was formed. Dilution with water yielded 2.9 g (74%) of 2,2-diiododimedone. Recrystallization from alcohol gave yellow, lustrous plates. The m.p. was 139-140°. 2,2-Diiododimedone is soluble in glacial acetic acid and ether, sparingly soluble in ethanol, and insoluble in water. It decomposed rapidly in light with liberation of iodine. The same compound was obtained by

the reaction of the dioxane complex of iodine chloride with dimedone itself. A mixed melting point of the 2,2-diiododimedone samples obtained by these two methods was not depressed.

Found %: I 64.97; 64.83. $C_8H_{10}O_2I_2$. Calculated %: I 64.74.

Reaction of sodium dimedone-2-sulfonate with diazotized aniline. To a diazotized solution of aniline (0.93 g of aniline in 7.5 ml of 10% hydrochloric acid and 0.93 g of sodium nitrite in 6 ml of water) at pH 4-5 was added a solution of 2.42 g of sodium dimedone-2-sulfonate in 25 ml of glacial acetic acid. After 2 hr, the precipitate of 2-phenylhydrazonodimedone was collected and recrystallized from alcohol. We obtained 1.6 g (65%) of orange crystals of 2-phenylhydrazonodimedone. The m.p. was 142° (142° [26]). The same product was obtained by coupling in neutral and alkaline media. Coupling sodium dimedone-2-sulfonate with diazotized p-nitroaniline yielded 2-(p-nitrophenylhydrazono)-dimedone (34%). The m.p. was 215° (215-217° [27]).

Imine of ammonium dimedone-2-sulfonate (V). A mixture of 8 g of ammonium acetate, 9 ml of glacial acetic acid, and 2.42 g of sodium dimedone-2-sulfonate was heated for 1 hr. The homogeneous solution crystallized on cooling. The crystals were washed several times with cold 60% alcohol to yield 1.2 g (51%) of the imine of ammonium dimedone-2-sulfonate. The white crystals obtained by recrystallization from dilute ethanol were soluble in water and glacial acetic acid, sparingly soluble in ethanol, and insoluble in ether. The m.p. was 332-335° (decomp.).

Found %: N 11.93. $C_8H_{16}O_4N_2S$. Calculated %: N 11.85.

Bromination of the imine of ammonium dimedone-2-sulfonate. To a solution of 1.18 g of the imine of ammonium dimedone-2-sulfonate in 5 ml of 50% ethanol was slowly added bromine water until it was completely decolorized. The 0.9 g (61%) of 2,2-dibromodimedone, which precipitated, was recrystallized from carbon tetrachloride. The m.p. was 143° (144° [25]).

Phenylimine of aniline dimedone-2-sulfonate (VIII). The reaction was carried out analogously to the preparation of substance (V), but 3 ml of aniline was used instead of ammonium acetate. We obtained 3 g (77.5%) of the phenylimine of aniline dimedone-2-sulfonate. The product was recrystallized from ethanol. The white, finely crystalline substance was soluble in ethanol and glacial acetic acid and almost insoluble in cold water, ether and nonpolar solvents. The m.p. was 171°.

Found %: N 6.79, 7.71. $C_{20}H_{22}O_4N_2S$. Calculated %: N 7.21.

Anilide of dimedone-2-sulfonic acid (X). A mixture of 2.2 g of dimedone-2-sulfonic acid and 4.5 ml of thionyl chloride was heated in a flask with a reflux condenser on a water bath at 65-75° for 4 hr. The excess thionyl chloride was removed in a water pump vacuum. The residual oily substance was dissolved in 20 ml of anhydrous ether and 2 ml of aniline in 10 ml of anhydrous ether added. There was a vigorous reaction and a white substance precipitated. The mixture was treated with 10 ml of ethanol in the cold and the solution filtered. Removal of the ethanol and recrystallization of the residue from ethanol yielded 0.46 g (16%) of the anilide of dimedonesulfonic acid. The product was soluble in alcohol and water and insoluble in benzene, ether, and chloroform. The m.p. was 188°.

Found %: N 4.94. $C_{14}H_{17}O_4NS$. Calculated %: N 4.75.

The ethanol-insoluble residue was aniline dimedonesulfonate. It had m.p. 199°. It did not depress the melting point of aniline dimedone-2-sulfonate obtained from the acid and aniline. The anilide of dimedone-2-sulfonic acid was also obtained in small amounts (20%) by treatment of sodium dimedone-2-sulfonate with phosphorus pentachloride and subsequent treatment with aniline.

Methyl dimedone-2-sulfonate (XI). A solution of diazomethane (obtained from 8 g of N nitrosomethylurea) was added from a dropping funnel with vigorous stirring and cooling to a suspension of 3.3 g of dimedone-2-sulfonic acid in 30 ml of ether until the ether in the flask had a yellow color from excess diazomethane and evolution of nitrogen ceased. The precipitate formed was recrystallized from ligroin to give 3.1 g (88.5%) of methyl dimedone-2-sulfonate. The product was readily soluble in water, ethanol, benzene, and chloroform and insoluble in ether. It had m.p. 69-70°.

Found %: S 13.71. $C_9H_{14}O_5S$. Calculated %: S 13.65.

Ammonium salt of methyl dimedone-2-sulfonate (XII). This product was obtained in 95% yield by introduction of dry ammonia into a solution of 1.17 g of methyl dimedone-2-sulfonate in 8 ml of anhydrous ethanol.

Recrystallization from methanol yielded a white, crystalline substance. It was soluble in water, sparingly soluble in ethanol, and insoluble in ether and benzene. The m.p. was 173-174°.

Found %: N 5.38. $C_9H_{17}O_5SN$. Calculated %: N 5.58.

SUMMARY

1. Sodium dimedone-2-sulfonate reacts with electrophilic reagents (nitric acid, bromine, sulfuryl chloride, iodine chloride, and aryl diazo compounds) with the loss of the sulfonic acid group and forms the corresponding derivatives of dimedone.

2. The reaction of sodium dimedone-2-sulfonate in glacial acetic acid with ammonium acetate yielded the imine of ammonium dimedone-2-sulfonate and the reaction with aniline gave the phenylimine of aniline dimedone-2-sulfonate. The structure of these compounds was confirmed by infrared spectra.

3. Dimedonesulfonyl chloride was not isolated in a pure form, but its existence was demonstrated by preparation of the anilide.

4. The action of diazomethane on dimedone-2-sulfonic acid yielded the methyl ester, which reacted with ammonia to give the ammonium salt of the enol form. The infrared absorption spectra of these compounds were plotted.

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RADICAL REACTIONS OF PERCARBONATES

I. THERMAL DECOMPOSITION OF DIBENZYL AND DICYCLOHEXYL PEROXYDICARBONATES IN BENZENE AND ISOPROPANOL

G. A. Razuvaev and L. M. Terman

Gor'kii State University
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2387-2393,
July, 1960
Original article submitted August 31, 1959

Much attention has been paid to the reactions of free alkyl radicals and they have been studied quite well. The reactions of simple oxygen-containing radicals of the type RO· have been described comparatively little in the literature and most of the investigations have been concerned with their behavior in the gas phase. A convenient subject for the study of such radicals in solution is the decomposition of percarbonates, which proceeds according to the scheme:

$$ROC(=O)-O-C(=O)OR \rightarrow 2ROC(=O)O\cdot \quad (1)$$

$$ROC(=O)O\cdot \rightarrow RO\cdot + CO_2 \quad (2)$$

Diethyl peroxydicarbonate was first synthesized by Wieland [1] by the reaction:

$$C_2H_5OC(=O)Cl + Na_2O_2 \rightarrow \left(C_2H_5OC(=O)O\right)_2 + 2NaCl$$

Strein et al. [2] synthesized a large group of percarbonates by an analogous method and studied the thermal decomposition of pure diethyl and diisopropyl peroxydicarbonates in the absence of solvent by passing them through a tube heated with steam. The decomposition of diisopropyl percarbonate yielded (in moles per mole of peroxide): isopropanol 0.91, acetone 0.42, CO_2 1.61, acetaldehyde 0.45, and ethane 0.41. Equations (1-3) were put forward as the decomposition scheme.

$$(CH_3)_2CHO\cdot + \left[(CH_3)_2CHOC(=O)O\right]_2 \rightarrow (CH_3)_2CHOH + (CH_3)_2CO + 2CO_2 + (CH_3)_2CHO\cdot \quad (3)$$

It is evident that radicals formed during the thermal decomposition of the peroxide attack molecules of undecomposed peroxide. The products of this reaction are isopropanol, acetone, and carbon dioxide. The radicals $(CH_3)_2CHO\cdot$ may also decompose to give methyl radicals, which then dimerize to ethane, and acetaldehyde. The decomposition kinetics, which were studied in dilute solutions in toluene and 2,2-oxodiethylenebisallyl carbonate, showed that the rate constant of the decomposition corresponds to an equation of the first order (relative to the peroxide concentration) and the over-all activation energy of the process equals 30.0 kcal/mole for diethyl peroxydicarbonate and 28.1 kcal/mole for diisopropyl peroxydicarbonate. Strein also showed percarbonates may be

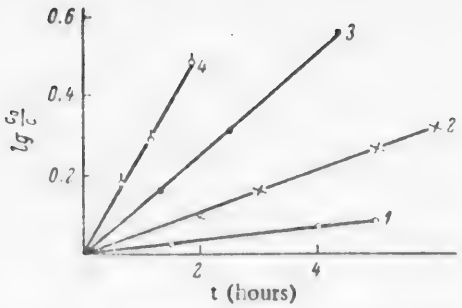

Fig. 1. Decomposition of dibenzyl peroxydicarbonate in benzene. Lines 1, 2, 3, and 4 obtained at 45, 50, 55 and 60°, respectively; C_0= 0.075 mole/liter.

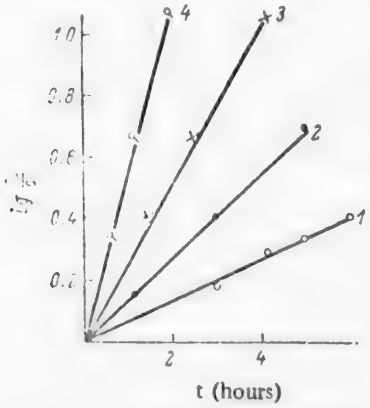

Fig. 2. Decomposition of dicyclohexyl peroxydicarbonate in benzene. Lines 1, 2, 3, and 4 were obtained at 45, 50, 55, and 60°, respectively; C_0= 0.075 mole/liter.

used successfully as initiators of polymerization reaction [2, 3].

In the same year, Cohen and Sparrou [4] published the results of an investigation of the thermal decomposition of diisopropyl percarbonate in ethylbenzene. They isolated carbon dioxide (1.76 mole per mole of peroxide), 2,3-diphenylbutane (the dimerization product of radicals from the solvent), and isopropanol in a yield of only 1.18 mole per mole of peroxide. Acetone was not isolated. The amount of isopropanol, which was less than the amount required by theory, (2 mole per mole of peroxide) and the absence of acetone from the reaction products hampered the interpretation of the mechanism. It seemed interesting to us to make a more thorough investigation of problems associated with the behavior of percarbonates in different solvents.

In the present work, we report the results of a study of the thermal decomposition of dibenzyl and dicyclohexyl peroxydicarbonates in benzene and isopropanol. It was found that the kinetics of the decomposition of dibenzyl and dicyclohexyl percarbonates in benzene at 45, 50, 55, and 60° (±0.05°) and a peroxide concentration of 0.075 mole/liter corresponded to the equation of a first order reaction with respect to peroxide.

The numerical values of the rate constant for each individual case were determined from the slope of the line drawn through the experimental points which were plotted in the coordinates of log c_0/c against t (Figs. 1 and 2) where c_0 is the initial peroxide concentration and c its concentration at time t. The experimental points lay close to the line, which gives grounds for considering that the reaction was first order with respect to peroxide in both cases.

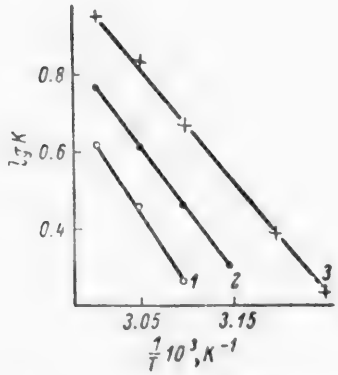

Fig. 3. Temperature dependence of decomposition rate of percarbonates. Lines 1 and 2 are for dibenzyl peroxydicarbonate and dicyclohexyl peroxydicarbonate in benzene; line 3 is for dibenzyl peroxydicarbonate in benzyl alcohol.

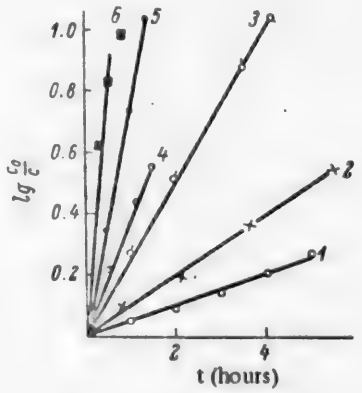

Fig. 4. Decomposition of dibenzyl peroxydicarbonate in benzyl alcohol. Lines 1, 2, 3, 4, 5, and 6 were obtained at 35, 40, 45, 50, 55, and 60°, respectively; C_0= 0.073 mole/liter.

Temperature	dicyclohexyl peroxydicarbonate in benzene	dibenzyl peroxydicarbonate in benzene	dibenzyl peroxydicarbonate in dibutyl phthalate	dibenzyl peroxydicarbonate in benzyl alcohol
35°	–	–	–	2.93
40	–	–	–	5.9
45	4.15	1.1	1.75	15.57
50	8.46	3.19	3.0	22.36
55	16.28	8.3	7.5	47.9
60	34.8	17.97	13.25	80.9
E $\frac{(kcal)}{(mole)}$	29.7	31.8	32.1	26.8

We calculated the apparent activation energy of the decomposition of peroxides in benzene from the slope of lines in the coordinates of log k against 1/T (Fig. 3, lines 1 and 2). The numerical values of the rate constants of percarbonate decomposition and the apparent activation energies are given in the table.

It would have been interesting to study the kinetics of percarbonate decomposition in isopropanol, but this was impossible due to the extremely low solubility of peroxides in the alcohol. We obtained data on the kinetics of decomposition of dibenzyl percarbonate in benzyl alcohol. The peroxide decomposed rapidly in it at low temperatures. As Fig. 4 shows, the experimental points lay well on a line and the rate constants, calculated from the slopes of the line, were almost a whole order higher than the rate constants for the decomposition of percarbonates in benzene at the same temperatures (Table 1). The apparent activation energy calculated for this case (Fig. 3, line 3) equalled 26.8 kcal/mole, i.e., 5 kcal/mole lower than the activation energy for decomposition in benzene. This indicates that in the decomposition of peroxides in alcohols, the solvent plays an active part in the reaction. Secondary radicals formed from solvent molecules on their dehydrogenation by peroxide radicals initiate the decomposition of peroxide and due to this, the over-all rate of decomposition is increased. These kinetic data are well confirmed by investigations of the decomposition products of peroxides in benzene and isopropanol. The following products were isolated from decomposition in isopropanol (in moles per mole of peroxide): carbon dioxide 1.9, cyclohexyl or benzyl alcohol 1.685–1.74, acetone 0.9, and an unidentified product (A) which appeared as a viscous yellow oil, 5% of the weight of peroxide taken. Thermal decomposition of percarbonates in benzene yielded the following (in moles per mole of peroxide taken): CO_2 1.8, corresponding alcohol 0.98, cyclohexanone or benzaldehyde 0.22–0.25, and product (A) 22% of the weight of peroxide taken. Biphenyl, which could have been formed due to dimerization of phenyl radicals formed by abstraction of hydrogen from benzene molecules, was not found. The fact that less than the expected amount of carbonyl compound (benzaldehyde or cyclohexanone) was obtained (0.22–0.25 mole /mole of peroxide instead of 1 mole /mole peroxide) compels us to assume that under the action of the unconsumed peroxide, this compound underwent condensation processes analogous to the reactions described in the literature for benzaldehyde and this gave a considerable yield of diphenylethylene glycol dibenzoate [8, 9]. To check this hypothesis, we carried out an experiment with a definite amount of cyclohexanone added to the reaction mixture before the beginning of decomposition. At the end of the reaction, 30% of the cyclohexanone taken was found. A product was isolated in the form of a viscous yellow oil. Elementary analysis data and the hydrolysis number of the product obtained during decomposition of dibenzyl percarbonate were close to the values calculated for diphenylethylene glycol dibenzoate (see Experimental). In addition, the weight of oil isolated corresponded well to the unaccounted amount of carbonyl compound. This product was not studied in detail.

Thus, the first act in the decomposition of percarbonates in solvents is cleavage of the peroxide molecule at the O - O bond with subsequent liberation of carbon dioxide and the formation of RO· radicals (equations 1 and 2). It might have been expected that the RO· radicals formed would have reacted in the three following directions:

$$C_6H_5CH_2O\cdot \longrightarrow C_6H_5\cdot + CH_2O, \quad (4)$$

$$C_6H_5CH_2O\cdot + HR \longrightarrow C_6H_5CH_2OH + R\cdot, \quad (5)$$

$$C_6H_5CH_2O\cdot + C_6H_5CH_2O\cdot \longrightarrow C_6H_5C\langle{}^{O}_{H} + C_6H_5CHOH\cdot \quad (6)$$

In our experiments, we did not detect the direct decomposition (4), though it is known for many other RO· radicals [2, 6, 7, 8]. The data obtained indicate that under the conditions of our experiments (concentrations

0.145 -0.285 M, 50-60°), cyclohexyloxy and benzyloxy free radicals react only according to schemes (5) and (6). Had the percarbonates reacted solely with abstraction of hydrogen from the solvent during decomposition in isopropanol, we should have obtained 2 moles of alcohol ROH per mole of peroxide decomposed according to equation (V). The cyclohexanone (or benzaldehyde) (0.03 mole per mole of peroxide) and product (A) (5% of the peroxide weight) found in the reaction products indicate that in addition to the main process of solvent dehydrogenation, there was also disproportionation of (VI) or (III). The absence of products from reaction with the solvent during the decomposition of percarbonates in benzene and also the fact that studying the kinetics of percarbonate decomposition in such an inert solvent as dibutyl phthalate gave values for the rate constants and apparent activation energy which coincided with the values for decomposition in benzene (table) indicate that the reaction of radicals generated from the peroxide probably proceeds in a "cage" of solvent. This may explain the fact that RO· radicals have a considerably lower activity than alkyl free radicals in the abstraction of hydrogen from a solvent, as was also reported by McBay [5].

Thus, the thermal decomposition of percarbonates in solution liberates carbon dioxide and forms radicals of the type RO·, which undergo conversion in two ways, depending on the solvent: either dehydrogenate the solvent, as was demonstrated for decomposition in isopropanol, or disproportionate, as was demonstrated for decomposition in benzene.

EXPERIMENTAL

The solvents were absolutely dry and pure in all experiments. The isopropanol, which was dried by the procedure in [10] and distilled, had b.p. 82.2°, n_D^{20} 1.3775. However, it was found that it contained a certain amount of acetone. The latter was determined quantitatively and allowed for in calculating the acetone in each experiment. Cryoscopic grade benzene was distilled over metallic sodium; b. p. 80.1, n_D^{20} 1.500.

Dibenzyl and dicyclohexyl peroxydicarbonates were synthesized by the procedure in [2], purified by reprecipitation from acetone with water, and dried in vacuum at room temperature. In contrast to low-molecular percarbonates, dibenzyl and dicyclohexyl peroxydicarbonates were quite stable and could be stored in a refrigerator (+ 5°) for several months without decomposition. A product containing a 100% peroxide was used for the reaction.

The decomposition was carried out in a round-bottomed flask with a reflux bulb condenser attached with a ground joint. For trapping the carbon dioxide, a system of potash bulbs with 30% KOH solution was connected to the top of the condenser. The decomposition was carried out at 60-70° in a stream of dry nitrogen for 50 hr (the time was established empirically from a negative reaction for peroxide).

Thermal Decomposition of Peroxydicarbonates in Isopropanol*

The decomposition of dicyclohexyl peroxydicarbonate was carried out in solution with peroxide concentrations of 0.145 and 0.275 M. At the end of the reaction, the amount of carbon dioxide liberated was determined from the increase in weight of the potash bulbs. It was found, however, that vapor of low-boiling acetone penetrated into the potash bulbs. The amount of it was determined gravimetrically with 2,4-dinitrophenylhydrazine and allowed for in the calculation of acetone and CO_2 in each experiment. The hydrazone melted at 126°, and a mixed melting point with the 2,4-dinitrophenylhydrazone of pure acetone was not depressed. The solvent was distilled from the reaction mixture on a water bath. Acetone was identified in the first fraction (57-82°) from the derivative with 2,4-dinitrophenylhydrazine. The melting point of the derivative was 126° and a mixed melting point with the derivative of pure acetone was not depressed. The amount of acetone was determined by oxime formation [11]. The residue after distillation of the first fraction was vacuum distilled until all the isopropanol had been removed. The completeness of removal of isopropanol was checked by separation of the residue after distillation on a chromatography column. Isopropanol was not found.

The residue after distillation of isopropanol was found to contain cyclohexanol, cyclohexanone, and about 5% of an unidentified product, which corresponded to about 5% of the weight of peroxide taken. The cyclohexanol was identified by the derivative with α-naphthyl isocyanate. The m.p. was 128° and a mixed melting point was not depressed. The amount of cyclohexanol was determined by acetylation [12]. Cyclohexanone was identified as the 2,4-dinitrophenylhydrazone. The m.p. was 162° and a mixed melting point was not depressed. The cyclohexanone was determined quantitatively by the bisulfite method. The residue after removal of samples for cyclohexanol and cyclohexanone was weighed and dissolved in diethyl ether to decrease the loss during subsequent treatment. The ether solution was repeatedly washed with water to remove cyclohexanol and then the cyclohex-

*M. E. Pudeeva helped with the work.

anone precipitated with sodium bisulfite. The derivative was collected on a Schott filter and washed with ether. The filtrate was washed with water and dried over baked Na_2SO_4 and then the ether removed by distillation. A viscous yellow oil was isolated.

Decomposition of dibenzyl peroxydicarbonate. It was found that dibenzyl percarbonate is very sparingly soluble in isopropanol (0.004 mole/liter); in an experiment with this peroxide concentration, it was possible to isolate only acetone as its 2,4-dinitrophenylhydrazone. The m.p. was 126° and a mixed melting point was not depressed. The acetone was determined quantitatively by oxime formation [11]. An experiment was carried out with a peroxide concentration of 0.252 M. In this case, the undissolved peroxide lay on the bottom of the flask as a heavy, finely crystalline precipitate. The decomposition was carried out by the procedure described above. The following reaction products were found: 1) acetone; the 2,4-dinitrophenylhydrazone had m.p. 126° and a mixed melting point was not depressed; 2) benzyl alcohol was determined by acetylation [12]; the α-naphthylcarbamate had m.p. 134° and a mixed melting point was not depressed; 3) benzaldehyde identified as the 2,4-dinitrophenylhydrazone (m.p. 237°) and a mixed melting point was not depressed. The amount was determined by the bisulfite method [13]. The condensation product of benzaldehyde, which formed a viscous yellow oil, was isolated from the distillate after steam distillation of the reaction mixture. The elementary analysis data given below and the hydrolysis number of this product agree with values calculated for diphenylethylene glycol dibenzoate.

Found %: C 78.0; H 6.2. Hydrolysis number: 185. $C_{28}H_{22}O_4$. Calculated %: C 79.6; H 5.2. Hydrolysis number: 186.

Thermal decomposition of percarbonates in benzene. The decomposition of dibenzyl and dicyclohexyl percarbonates in benzene was carried out with concentrations of 0.25 M. After the benzene had been removed by distillation the decomposition products were analyzed by the procedure described above.

Kinetics of Percarbonate Decomposition

Ampoules were charged with 10-12 ml portions of peroxide solution (0.075 M). The ampoules were connected to a vacuum system, the solution frozen with a mixture of carbon dioxide and acetone, and the ampoules pumped out to high vacuum. The tap connecting the ampoules to the system was then closed and the solution allowed to warm up to room temperature. The ampoules were again immersed in a cooling mixture and the gas liberated was pumped off. This operation was carried out three times and then the ampoules were sealed off. All possibilities of the distillation of solvent during this procedure were excluded. The ampoules were placed in a thermostat and kept at a definite temperature for the required time and then they were removed, cooled, and opened. The contents of the ampoules were analyzed for peroxide content iodometrically [14].

SUMMARY

1. The thermal decomposition of dibenzyl and dicyclohexyl peroxydicarbonates in benzene and isopropanol was studied.

2. It was shown that radicals of the type RO· are formed during the thermal decomposition of percarbonate in solution. The radicals are capable of abstracting hydrogen from the solvent (decomposition in isopropanol) or disproportionating (decomposition in benzene).

3. The fall in concentration of percarbonates during their decomposition in solvents obeys the kinetic law of a first order reaction and the apparent activation energy depends on the nature of the solvent.

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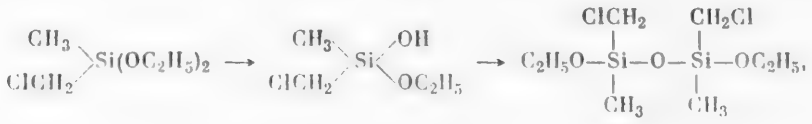
METHODS OF SYNTHESIZING 1, n-DIETHOXYMETHYLCHLOROMETHYLSILOXANES AND SUBSTITUTIONS OF THE CHLORINE IN THE α-CHLOROMETHYL GROUP

K. A. Andrianov and L. M. Volkova

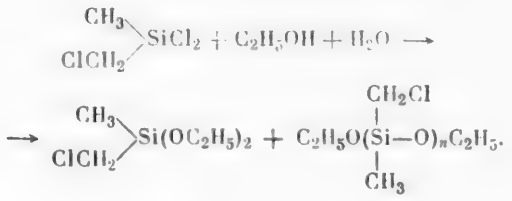
Institute of Heteroorganic Compounds, Academy of Sciences of the USSR

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2392-2397, July, 1960
Original article submitted July 1, 1959

Polyorganosiloxanes with polar groups in the organic radicals are attracting the attention of investigators. In the present work we synthesized low-molecular 1,n-diethoxymethylchloromethylsiloxanes, containing chloromethyl groups in addition to the terminal ethoxyl groups, and studied the reaction of chlorine in the α-chloromethyl group with aniline. The diethoxymethylchloromethylsiloxanes were synthesized by two methods: 1) by hydrolysis of methylchloromethyldiethoxysilane with a small amount of water according to the reaction:



2) by the direct action of 99% alcohol on methylchloromethyldichlorosilane:

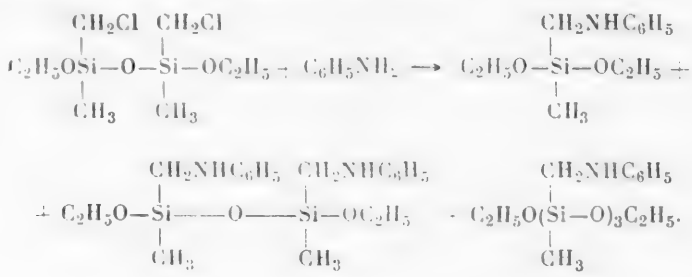


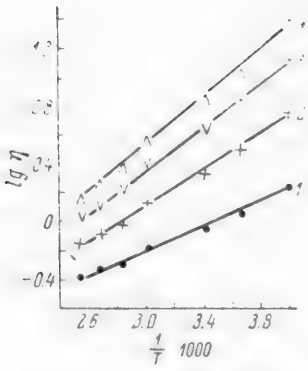
These reactions yielded 1,n-diethoxymethylchloromethylsiloxanes with the general formula $C_2H_5O\left(\begin{array}{c}CH_2Cl\\|\\Si-O\\|\\CH_3\end{array}\right)_n C_2H_5$ with a degree of polymerization n = 2, 3, or 4. The properties of the substances obtained are given in the table.

The viscosities of the compounds obtained were determined at different temperatures (figure). All the 1,n-diethoxymethylchloromethylsiloxanes studied showed a linear relation between the logarithm of the viscosity and $1/T^0$. Calculation of the activation energy of viscous flow showed that it equalled 2.656 (when n = 2) and 3.613 kcal/mole (n = 4), which is considerably higher than the activation energy of the series $(CH_3)_3SiO[Si(CH_3)_2O]_n \cdot Si(CH_3)_3$ with the same degree of polymerization [1]. This shows that the chloromethyl group and the terminal ethoxy groups increase the strength of the intermolecular reaction. Together with replacement of chlorine by the

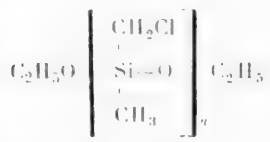
Substance	Formula	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	Activation energy of viscous flow at 20-120° (kcal/mole)	MR	
						found	calculated
1,2-Di-(chloromethylmethylethoxy)-disiloxane	CH_2Cl | $C_2H_5O(Si-O)_2C_2H_5$ | CH_3	108-109° (8)	1.4320	1.097	2.656	68.79	69.47
1,2,3-Tri-(chloromethylmethyl)-1,3-diethoxytrisiloxane	CH_2Cl | $C_2H_5O(Si-O)_3C_2H_5$ | CH_3	100 (2)	1.4420	1.137	3.302	93.01	93.03
1,2,3,4-Tetra-(chloromethylmethyl)-1,4-diethoxytetrasiloxane	CH_2Cl | $C_2H_5O(Si-O)_4C_2H_5$ | CH_3	114-115 (1)	1.4470	1.170	3.613	116.1	116.57

phenylamino group, the reaction of aniline with bis(chloromethylethoxy)disiloxane resulted in the formation of substances with different molecular weights and phenylaminomethylmethyldiethoxysilane and 1,2,3-tri(phenylaminomethylmethyl)-1,3-diethoxytrisiloxane were isolated. These substances could only have been formed as a result of rearrangement involving rupture of the Si–O–Si bond and transfer of the ethoxyl group under the action of aniline. The over-all equation of the reaction is as follows:



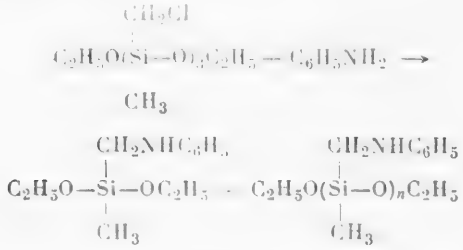


Temperature dependence of the logarithm of the viscosity for



Values of n: 1) 1, 2) 2, 3) 3, 4) 4.

Analogously, the reaction of 1,2,3-tri(chloromethylmethyl)-1,3-diethoxytrisiloxane with aniline yielded phenylaminomethylmethyldiethoxysilane and a very viscous polymer, which could not be distilled in vacuum.



EXPERIMENTAL

Etherification of chloromethylmethyldichlorosilane. Into a reaction flask was placed 355 g of chloromethylmethyldichlorosilane, 220 g of ethanol added from a dropping funnel over a period of 40 min, and the reaction mixture heated at 75-80° with stirring for 10 hr. Distillation of the product yielded 280 g (70%) of chloromethylmethyldiethoxysilane with b.p. 162–165°, n_D^{20} 1.4145, d_4^{20} 0.998; and 78 g of residue.

Isolation of 1,n-diethoxymethylchloromethylsiloxanes. The still residues from several experiments were combined and vacuum distilled. From 400 g of still residues were isolated the following products: 1) 43.5 g (10.8%) of chloromethylmethyldiethoxysilane with b.p. 48-50° (8 mm), n_D^{20} 1.4150, d_4^{20} 0.999.

2) 160 g (40%) of 1,2-di(chloromethylmethylethoxy) disiloxane with b.p. 106-109° (8 mm); after redistillation, the substance had b. p. 108-109° (8 mm), n_D^{20} 1.4320, d_4^{20} 1.097, MR 68.79; Calc. 69.47.

Found %: C 32.95, 33.11; H 6.90, 7.07; Cl 24.61, 24.71; Si 19.0. M 296. $C_8H_{20}O_3Si_2Cl_2$. Calculated %: C 32.99; H 6.87; Cl 24.39; Si 19.25. M 291.

3) 73 g (18.3%) of 1,2,3 tri(chloromethylmethyl)-1,3-diethoxytrisiloxane with b.p. 145-152° (7 mm); after redistillation, the substance had b.p. 100° (2 mm), n_D^{20} 1.4420, d_4^{20} 1.137, MR 93.01; Calc. 93.03.

Found %: C 30.02, 30.21; H 6.76, 6.86; Cl 26.81, 26.85; Si 20.95, 20.85. $C_{10}H_{25}O_4Si_3Cl_3$. Calculated %: C 30.02; H 6.26; Cl 26.66; Si 21.00.

4) 14 g (3.5%) of 1,2,3,4-tetra(chloromethylmethyl)-1,4-diethoxytetrasiloxane with b.p. 181-184° (7 mm); after redistillation, the substance had b.p. 114–115° (1 mm), n_D^{20} 1.4470, d_4^{20} 1.170, MR 116.1; Calc. 116.57.

Found %: C 28.76, 28.86; H 5.85, 5.64; Cl 27.70, 27.51; Si 21.67, 21.70. $C_{12}H_{30}O_5Si_4Cl_4$. Calculated %: C 28.34; H 5.91; Cl 27.41; Si 22.0.

Hydrolysis of chloromethylmethyldiethoxysilane. 1) Into a flask was placed 44.5 g of chloromethylmethyldiethoxysilane and 18.0 g of 96% alcohol containing 1.3 g of water added over a period of 1.5 hr with stirring at 60-80°. The reaction mixture was stirred 2 hr, the alcohol removed by distillation, and the residue vacuum distilled to yield 13.5 g (30.4%) of starting chloromethylmethyldiethoxysilane and 12.4 g (34.8%) of bis(chloromethylmethylethoxy)disiloxane with b.p. 106–108° (8 mm), n_D^{20} 1.4330, d_4^{20} 1.098, MR 68.77.

2) Analogously, the hydrolysis of 149 g of chloromethylmethyldiethoxysilane with 36 g of 75% alcohol containing 9 g of water yielded: a) 4.5 g of starting chloromethylmethyldiethoxysilane with b.p. 45–48° (8 mm), n_D^{20} 1.4150, d_4^{20} 0.998; b) 17.7 g of 1,2-di(chloromethylmethylethoxy)disiloxane with b.p. 104–107° (8 mm), n_D^{20} 1.4320, d_4^{20} 1.096, MR 68.81; c) 18.8 g of 1,2,3-tri(chloromethylmethyl)-1,3-diethoxytrisiloxane with b.p. 107–110° (2mm), n_D^{20} 1.4430, d_4^{20} 1.139, MR 93.03; and d) 8.1 g of 1,2,3,4-tetra(chloromethylmethyl)-diethoxytetrasiloxane with b.p. 136–140° (2 mm), n_D^{20} 1.4490, d_4^{20} 1.180, MR 115.5.

Reaction of bis(chloromethylmethylethoxy)-disiloxane with aniline. A mixture of 43.6 g of bis(chloromethylmethylethoxy)-disiloxane and 94 g of aniline was heated at 110-120° and stirred for 4 hr. The reaction mixture was left to cool overnight. On the following day, the precipitate was collected and the filtrate distilled to yield: 1) 9.4 g of phenylaminomethylmethyldiethoxysilane.

B. p. 120–125° (7 mm), n_D^{20} 1.4975, d_4^{20} 1.002, MR 69.8; Calc. 69.03.

Found %: Si 11.74, 11.92, M 230. $C_{12}H_{21}C_2NSi$. Calculated %: Si 11.7. M 239.

2) 4.0 g of bis(phenylaminomethylmethylethoxy)disiloxane:

B.p. 215–225° (0.5 mm), n_D^{20} 1.5198, d_4^{20} 1.009.

Found %: N 6.59, 6.78; Si 14.8, 15.0; OC_2H_5 22.17. $C_{20}H_{32}O_5N_2Si_2$. Calculated %: N 6.93; Si 13.86; OC_2H_5 22.24.

3) 9.1 g of 1,2,3-tri(phenylaminomethylmethyl)-1,3-diethoxytrisiloxane:

B.p. 270–280° (0.5 mm), n_D^{20} 1.539, d_4^{20} 1.102, MR 161.5; Calc. 163.3.

Found %: N 7.97, 7.77; Si 16.38, 16.37; OC_2H_5 16.5. $C_{28}H_{43}O_4N_3Si_3$. Calculated %: N 7. 38; Si 14.76; OC_2H_5 15.8.

Reaction of 1,2,3-tri(chloromethylmethyl)-1,3-diethoxytrisiloxane with aniline. A mixture of 40 g of 1,2,3-tri(chloromethylmethyl)-1,3-diethoxytrisiloxane and 87 g of aniline was heated at 120-130° and stirred for 10 hr. The aniline hydrochloride was removed and the filtrate yielded 5 g of product with b.p. 70-80° (1 mm); after redistillation, the product had b.p. 135–140° (8 mm), n_D^{20} 1.4980, d_4^{20} 1.006, M 229, and was phenylaminomethylmethyldiethoxysilane. The residue was a clear, very viscous resin.

SUMMARY

1. New compounds of the general formula $C_2H_5O\left(Si(CH_2Cl)(CH_3)-O\right)_n C_2H_5 (n=2,3,4)$ were synthesized and their physical properties described.

2. The replacement of chlorine in the α-chloromethyl group of bis(chloromethylmethylethoxy)disiloxane and 1,2,3-tri(chloromethylmethyl)-1,3-diethoxytrisiloxane by aniline was studied and it was established that during the replacement of chlorine by a phenylaminomethyl group there is a rearrangement, accompanied by cleavage of the Si–O–Si bonds and exchange of ethoxyl groups.

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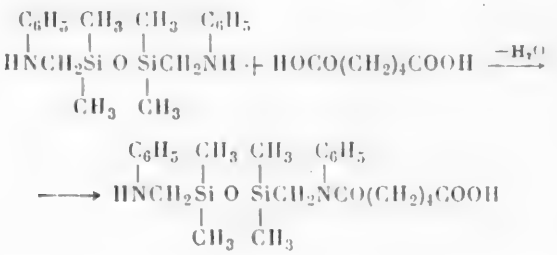
REACTIONS OF BIS (PHENYLAMINOMETHYL) TETRAMETHYLDISILOXANE WITH ACIDS

K.A. Andrianov and L. M. Volkova

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2397-2400, July, 1960
Original article submitted July 1, 1959

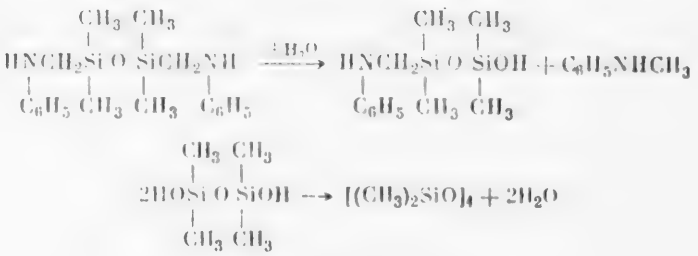
The literature contains very few data on the reactions of organosilicon amines with acids. Speck described polyamides obtained by the reaction of bis(p-aminomethylphenyl)dimethylsilane with three silicoorganic acids. He reported that the water liberated during the reaction may produce some cleavage of the Si–C bond. We investigated the reaction of bis(phenylaminomethyl)-tetramethyldisiloxane with adipic, phthalic, succinic, and fumaric acids. Our experiments showed that the condensation of bis(phenylaminomethyl) tetramethyldisiloxane with adipic acid at 150° both at atmospheric pressure and in vacuum proceeds very slowly. After 10 hr, no volatile reaction products could be collected apart from insignificant drops of liquid, which condensed on the walls of the condenser. Further experiments on the condensation of bis(phenylaminomethyl) tetramethyldisiloxane with the acids given above were carried out at 250 and 300° in a stream of nitrogen. When bis(phenylaminomethyl) tetramethyldisiloxane was heated at 250° with adipic acid, the liberation of a small amount of water was observed and then, as the mixture was heated, a water immiscible product collected in the receiver. This product distilled in considerable amounts. Investigation of the reaction products formed showed that they were a mixture of hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and methylaniline. All these products were identified. Very little water was liberated. The condensation product was a viscous liquid, containing a small amount of silicon (3-5%), or a solid, low-melting resin, which did not contain silicon (if the reaction was continued until the distillation of volatile products ceased). An analogous process occurred in the condensation of bis(phenylaminomethyl) tetramethyldisiloxane with other acids, such as terephthalic, succinic, and fumaric. The experimental data obtained show that the reaction between the secondary amine bis(phenylaminomethyl) tetramethyldisiloxane and the dibasic organic acids is complex and does not lead to organosilicon polyamides, but involves the development of a reaction with subsequent rupture of Si–C and Si–O–Si bonds:



The water liberated during the reaction reacts at high temperature with the reaction products or bis(phenylaminomethyl) tetramethyldisiloxane and this leads to rupture of the Si–C bond (see scheme below).

Together with octamethylcyclotetrasiloxane, hexamethylcyclotrisiloxane was formed and its formation involved rupture of the Si–O–Si bond. The undistillable reaction products were difficultly separable mixtures,

which were viscous or solid at room temperature. They were probably products from the reaction of methylaniline and the acids.



EXPERIMENTAL

Preparation of bis(phenylaminomethyl) tetramethyldisiloxane. Into a reaction flask was placed 390 g of aniline, 93 g of chloromethyldimethylchlorosilane added with stirring over a period of 40 min, and the mixture heated at 130-140° for 5 hr and left to cool overnight. On the following day, 200 ml of water and 100 g of 50% aqueous sodium hydroxide solution were added, the mixture was stirred for 2 hr at 50°, and the upper layer separated and distilled to yield 305 g of aniline and 86 g (75%) of bis(phenylaminomethyl) tetramethyldisiloxane with b.p. 235-245° (13 mm). After redistillation, the product had:

B.p. 243–246° (14 mm), n_D^{20} 1.5400, d_4^{20} 1.0275, MR 104.9; Calc. 104.7.

Found %: N 8.16, 8.34; Si 16.02, 15.98. $C_{18}H_{28}ON_2Si_2$. Calculated %: N 8.14; Si 16.28.

Condensation of bis(phenylaminomethyl) tetramethyldisiloxane with adipic acid. Into a reaction flask were placed 13 g of bis(phenylaminomethyl) tetramethyldisiloxane and 5.5 g of adipic acid and the mixture stirred and heated at 250° in a nitrogen atmosphere for 5 hr. There distilled 6.2 g of substance (n_D^{20} 1.4258), containing a drop of water; the residue in the flask consisted of a dark, viscous polymer, containing 4% of silicon. The reaction products liberated were dissolved in ether, washed three times with 1 N HCl and water, dried over $CaCl_2$, and distilled to yield the following fractions: 1st b.p. 130–135°, 1.0 g; 2nd b.p. 135–170°, 1.0 g; 3rd b.p. 170–175°, 1.2 g; residue 0.2 g. The first fraction was hexamethylcyclotrisiloxane. The crystals had m.p. 54–57°.

Found %: C 32.26, 32.35; H 8.11, 8.09; Si 37.03, 37.06. M 196. $C_6H_{18}O_3Si_3$. Calculated %: C 32.43; H 8.11; Si 37.83. M220.

The third fraction was octamethylcyclotetrasiloxane with n_D^{20} 1.3940, d_4^{20} 0.9550.

Found %: Si 37.36, 37.20. M 289. $C_8H_{24}O_4Si_4$. Calculated %: Si 37.83, M 296.

The wash waters were combined and evaporated to yield 1.2 g of a white crystalline substance, which was methylaniline hydrochloride with m.p. 121–123°.

Found %: Cl 24.8; Si none. $C_7H_{10}NCl$. Calculated %: Cl 24.6.

A mixture with authentic methylaniline hydrochloride had m.p. 122–124°.

Analogously, when a mixture of 26.1 g of bis(phenylaminomethyl) tetramethyldisiloxane and 11.1 g of adipic acid was heated at 250–300° for 10 hr, there distilled 18.5 g of product, which consisted of hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and methylamine; the distillation residue was a fusible, brittle resin, which did not contain silicon and was insoluble in alcohol and toluene.

Condensation of bis(phenylaminomethyl) tetramethyldisiloxane with terephthalic acid. A mixture of 13 g of bis(phenylaminomethyl) tetramethyldisiloxane and 6.6 g of terephthalic acid in a flask was stirred and heated in a nitrogen atmosphere. The liberation of volatile products began at 230° and 5 g of product distilled at 230–250° over a period of 4 hr; in the reaction flask there remained a viscous, heterogeneous resin, which contained 5.1% of silicon. More volatile products distilled with further heating and the silicon content of the distillation residue fell to 3.8%. The distilled products were treated with HCl solution, washed with water, dried over $CaCl_2$, and distilled. We isolated: 1) 1 g of hexamethylcyclotrisiloxane with b.p. 130–140°, which formed crystals with m.p. 56–58° and contained 37.2% of silicon; 2) 1 g of octamethylcyclotetrasiloxane with b.p. 170–175°, n_D^{20}

1.3945, d_4^{20} 0.9550. Methylaniline hydrochloride (2.1 g) was isolated from the aqueous layer.

Condensation of bis(phenylaminomethyl) tetramethyldisiloxane with fumaric and succinic acids. Into a reaction tube were placed 3.4 g of bis(phenylaminomethyl) tetramethyldisiloxane and 1.18 g of succinic acid; the distillation of volatile products began at 180° and there distilled 0.6 g of substance containing 19.5% of Si and having n_D^{20} 1.4280. The distillation residue formed layers on cooling; the upper layer was light in color and contained 32.8% of Si, while the lower layer was dark and viscous and contained 0.97% Si. Analogously, when 3.4 g of bis(phenylaminomethyl) tetramethyldisiloxane was heated with 1.16 g of fumaric acid, there distilled 0.6 g of product with n_D^{20} 1.4290 and containing 19.24% of silicon; the distillation residue consisted of two layers: the upper light layer (0.4 g) contained 28.3% of Si and the lower, dark layer contained 3.4% of Si.

SUMMARY

The reaction of bis(phenylaminomethyl) tetramethyldisiloxane with adipic, terephthalic, succinic, and fumaric acids was studied and it was shown that polyamides are not formed. The reaction involves cleavage of Si–C and Si–O–Si bonds. A reaction mechanism is proposed.

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CATALYTIC CONDENSATION OF AROMATIC KETONES WITH SCHIFF'S BASES FROM p-AMINOBENZOIC ESTERS AND AROMATIC ALDEHYDES

N. S. Kozlov and V. D. Pak

Perm Agricultural Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2400-2402, July, 1960
Original article submitted July 6, 1959

p-Aminobenzoic acid is known to have considerable and diverse physiological activity. In microorganisms, it plays the part of a growth vitamin. T. D. Mashkovskii [1] established that it very strongly depresses the growth of the bacteria of exanthematous fever and some Rickettsia. Many p-aminobenzoic esters such as anesthesine, novocaine, tutocaine, stovocaine, etc. have found wide application in medicine as local anesthetics [2]. I. N. Nazarov and N. S. Prostakov [3] synthesized esters of 4-aryl-4-piperidols and p-aminobenzoic acid, which have a very diverse physiological activity. K. S. Bokarev [4] described the synthesis of N-acyl derivatives of p-aminobenzoic acid and anthranilic acid in which the acyl groups were the residues of 2,4-dichloro- and 2,4,5-trichlorophenoxyacetic acids. These substances have growth regulating properties [5].

A. V. Stepanov [6] synthesized anesthesine N-glucosides of p- and o-aminobenzoic acids and their esters; M. Kh. Gluzman and V. I. Kovalenko [8] prepared N-quinovosyl-p-aminobenzoic acid. All these compounds are anesthetics.

The synthesis of alkyl and diethylaminoethyl esters of N-substituted p-aminobenzoic acid is described in the work of Epstein [9].

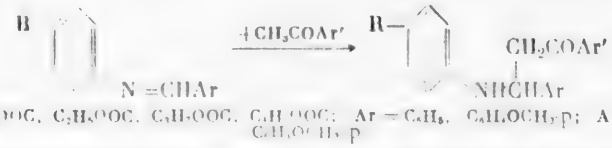
In the previous work of one of us [10], anesthesine was converted into the diethylidene compound by condensation with acetylene.

In the present work we undertook to synthesize new derivatives of p-aminobenzoic acid. For this purpose, we used a reaction we had studied previously. In the work of one of us [11, 12], a description was given of the catalytic condensation of Schiff's bases with aliphatic-aromatic ketones, which formed the corresponding β-arylamino ketones. In the present work, we used Schiff's bases from p-aminobenzoic esters.

From benzal methyl p-aminobenzoate and acetophenone, we synthesized β-(p-carbomethoxyanilino)-β-phenylpropiophenone (I); from benzal ethyl p-aminobenzoate and acetophenone, we synthesized β-(p-carboethoxyanilino)-β-phenylpropiophenone (II); from benzal n-propyl p-aminobenzoate and acetophenone, we obtained β-(p-carbopropoxyanilino)-β-phenylpropiophenone (III); from benzal n-butyl p-aminobenzoate and acetophenone, we obtained β-(p-carbobutoxyanilino)-β-phenylpropiophenone (IV). By condensing benzal methyl p-aminobenzoate with methoxyacetophenone, we obtained β-(p-carbomethoxyanilino)-β-phenyl-p-methoxypropiophenone (V); benzal ethyl p-aminobenzoate and methoxyacetophenone yielded β-(carboethoxyanilino)-β-phenyl-p-methoxypropiophenone (VI); benzal n-propyl p-aminobenzoate and methoxyacetophenone yielded β-(p-carbopropoxyanilino)-β-phenyl-p-methoxypropiophenone (VII); benzal n-butyl p-aminobenzoate and methoxyacetophenone yielded β-(p-carbobutoxyanilino) β-phenyl-p-methoxypropiophenone (VIII). Reaction of p-methoxybenzal methyl p-aminobenzoate and acetophenone yielded β-(p-carbomethoxyanilino)-β-p-methoxyphenylpropiophenone (IX); p-methoxybenzal ethyl p-aminobenzoate and acetophenone yielded β-(p-carbethoxyanilino)-β-

p-methoxyphenylpropiophenone (X); p-methoxybenzal n-propyl p-aminobenzoate and acetophenone yielded β-(p-carbopropoxyanilino)-β-p-methoxyphenylpropiophenone (XI). Condensation of p-methoxybenzal methyl p-aminobenzoate with methoxyacetophenone yielded β-(p-carbomethoxyanilino)-β-p-methoxyphenyl-p-methoxypropiophenone (XII); p-methoxybenzal ethyl p-aminobenzoate and methoxyacetophenone yielded β-(p-carboethoxyanilino)-β-p-methoxyphenyl-p-methoxypropiophenone (XIII); p-methoxybenzal n-propyl p-aminobenzoate and methoxyacetophenone yielded β-(p-carbopropoxyanilino)-β-p-methoxyphenyl-p-methoxypropiophenone (XIV); p-methoxybenzal n-butyl p-aminobenzoate and methoxyacetophenone yielded β-(p-carbobutoxyanilino)-β-p-methoxyphenyl-p-methoxypropiophenone (XV).

The synthesis of the compounds given above may be regarded as the result of the addition of the ketone molecule to the azomethine bond of the Schiff's base.



R = CH_3OOC, C_2H_5OOC, C_3H_7OOC, C_4H_9OOC; Ar = C_6H_5, $C_6H_4OCH_3$-p; Ar' = C_6H_5, $C_6H_4OCH_3$-p

Compound No.	R	R_1	R_2	Yield (%)	Melting point	% N calculated	% N found
(I)	CH_3OCO	H	H	51	184—185°	3.89	3.70, 3.73
(II)	C_2H_5OCO	H	H	38	148.5—150	3.75	3.89, 3.90
(III)	C_3H_7OCO	H	H	32	146.0—148	3.61	3.85, 3.61
(IV)	C_4H_9OCO	H	H	35	158.0—160	3.49	3.59, 3.68
(V)	CH_3OCO	H	OCH_3	49	175.0—176	3.59	3.74, 3.52
(VI)	C_2H_5OCO	H	OCH_3	29	131.0—133	3.47	3.35, 3.50
(VII)	C_3H_7OCO	H	OCH_3	33	124.5—126	3.35	3.42, 3.37
(VIII)	C_4H_9OCO	H	OCH_3	30.5	112.0—114	3.24	3.37, 3.44
(IX)	CH_3OCO	OCH_3	H	47	160.0—161.5	3.59	3.67, 3.62
(X)	C_2H_5OCO	OCH_3	H	45	163.0—165	3.47	3.66, 3.44
(XI)	C_3H_7OCO	OCH_3	H	37.5	141.0—142	3.35	3.60, 3.45
(XII)	CH_3OCO	OCH_3	OCH_3	39	143.0—145	3.34	3.59, 3.45
(XIII)	C_2H_5OCO	OCH_3	OCH_3	42	151—152	3.23	3.31, 3.29
(XIV)	C_3H_7OCO	OCH_3	OCH_3	34.5	139.0—141	3.11	3.20, 3.34
(XV)	C_4H_9OCO	OCH_3	OCH_3	49	107.0—109	3.03	3.10, 3.06

EXPERIMENTAL

The p-aminobenzoic esters were prepared according to data in [13, 14].

Synthesis of β-arylamino ketones. A 0.01 mole sample of Schiff's base was dissolved in 5-10 ml of alcohol with heating on a water bath. An equimolecular amount of aromatic ketone and 0.5-1 g of catalyst (hydrochloride of the amine used to prepare the Schiff's base) were then added. The reaction mixture was heated on a water bath for 5-15 min and then cooled. The crystals obtained were treated with ammonia and recrystallized from a mixture of toluene and alcohol or benzene and alcohol (sometimes from one solvent). The results obtained are given in the table.

SUMMARY

The condensation of Schiff's bases, obtained from p-aminobenzoic esters and aromatic aldehydes, with aliphatic-aromatic ketones was studied. Fifteen new β-arylamino ketones were synthesized. The reaction mechanism is examined.

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AUTOOXIDATION OF p-ETHYL-SEC-BUTYLBENZENE

S. V. Zavgorodnii and V. G. Shalganova

Voronezh State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2402-2406, July, 1960
Original article submitted June 7, 1959

The liquid-phase oxidation of dialkylbenzenes to hydroperoxides has not been studied sufficiently. There are mainly patent reports on this problem. Some investigations have been devoted to the autooxidation of cymenes [1-4], diisopropylbenzenes [5,6], and di-sec-butylbenzenes [7-9]. The autooxidation of p-ethylisopropylbenzene [6], p-isopropyl-tert-butylbenzene, p-methyl-sec-butylbenzene, and xylenes to the corresponding hydroperoxides has been studied [10].

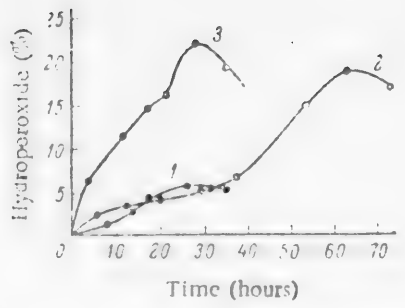
In the present work we studied the autooxidation of p-ethyl-sec-butylbenzene and p-sec-butylacetophenone by atmospheric oxygen in the presence of manganese resinate and some additives at 110°. It is generally accepted that in the autooxidation of alkylaromatic hydrocarbons, molecular oxygen first attacks tertiary alpha C atoms with the formation of hydroperoxides. Our investigations established that in the autooxidation of p-ethyl-sec-butylbenzene (I), the attack of molecular oxygen is directed predominantly toward the secondary alpha C atom of the ethyl radical with the formation of α-methyl-p-sec-butylbenzyl hydroperoxide (II) and it is only with prolonged autooxidation of hydrocarbon (I) or in the presence of cobalt acetate and sodium stearate that molecular oxygen attacks the tertiary alpha C atom of the sec-butyl radical with the formation of α-methyl-α-ethyl-p-ethylbenzyl hydroperoxide (III).

In contrast to p-diisopropylbenzene [5], hydrocarbon (I) is oxidized by atmospheric oxygen very slowly. As in the case of other hydrocarbons, the autooxidation proceeds in such a way that the hydroperoxide concentration first increases, reaches a maximum, and then begins to fall and with the prolonged passage of air, hydroperoxide disappears completely from the reaction mixture.

The curves in the figure show that during the autooxidation of (I) in the presence of manganese resinate alone (3 mg per mole), the maximum hydroperoxide concentration was reached after 27 hr and equaled 5.5%. Alkaline additives (sodium hydroxide and calcium hydroxide) did not accelerate the process appreciably, but stabilized it and made it possible to carry out the oxidation up to the formation of hydroperoxide at a higher concentration. Thus, when 0.18 mole of sodium hydroxide was added to the magnesium resinate, the maximum hydroperoxide concentration reached 18.4% after 64 hr. The oxidation of (I) was more efficient in the presence of manganese resinate and calcium hydroxide (0.6 mole). In this case, the maximum hydroperoxide concentration was 21.7% after 29 hr.

The main products from sulfuric acid cleavage of the hydroperoxide were p-sec-butylacetophenone (IV) and p-sec-butylphenol (V). Their yield for the best conditions was 14.8 and 3.9% respectively.

The autooxidation of (I) in the presence of manganese resinate and sodium hydroxide resulted in a maximum hydroperoxide concentration of 11.2% after 87 hr, which fell to 3.3% after 111 hr, and hydroperoxide disappeared completely from the reaction mixture after 125 hr. The oxidation products then were (IV), (V), and p-diacetylbenzene (VI). Their yields were 16.1, 3.4, and 0.08%, respectively. Thus, there was decomposition of the hydroperoxide simultaneously with its formation.



The autooxidation of (I) in the presence of manganese resinate, cobalt acetate, sodium stearate, calcium hydroxide, and sodium hydroxide proceeded quite vigorously, but the hydroperoxide concentration in the reaction mixture in this oxidation did not exceed 3.1%. After 133 hr, 82.7% of hydrocarbon (I) was oxidized. This yielded (IV), (VI) and p-acetylbenzoic acid (VII) in yields of 74.5, 8.3, and 1%, respectively. After 96 hr in the presence of the same initiators and additives, p-sec-butylacetophenone (IV) was oxidized to p-diacetylbenzene in 46.6% yield.

A characteristic of the oxidation of (I) was the fact that the main product was (IV) under different conditions. p-sec-Butylphenol was not isolated in experiments with cobalt acetate and sodium stearate.

EXPERIMENTAL

p-Ethyl-sec-butylbenzene (I) was obtained by alkylation of ethylbenzene with pseudobutylene in the presence of the catalyst $BF_3 \cdot H_3PO_4$ in molar ratios of 1.5: 1: 0.2 at 30° with an average yield of 77% [11]. Before oxidation, it was repeatedly treated with concentrated sulfuric acid, washed well with a 10% aqueous solution of sodium hydroxide and water, dried over NaOH, and distilled over metallic sodium. It had b.p. 205–207, d_4^{20} 0.8628, n_D^{20} 1.4925. The p-sec-butylphenol, which was used for identification of the oxidation products, was obtained by alkylation of phenol with pseudobutylene in the presence of the catalyst $BF_3 \cdot H_3PO_4$ [12]. It had m.p. 56–57°.

Autooxidation of p-ethyl-sec-butylbenzene

Into a glass column reactor in an oil thermostat were introduced substance (I), the initiators, and additives. The mixture was heated to 110° and air passed at 18 liter/hr until the maximum hydroperoxide concentration had been attained and the concentration began to fall or until the hydroperoxide disappeared from the reaction mixture completely. The hydroperoxide content of the reaction mixture was determined every 2-6 hr iodometrically.

Oxidation of (I) until hydroperoxide disappeared from the reaction mixture. The reactor was charged with 162 g of (I), 300 mg of sodium hydroxide, and 10 ml of methanol, the mixture heated to 70°, 3 mg of manganese resinate introduced, and dry air passed through the reaction mixture at 18 liter/hr. After 87 hr, the hydroperoxide concentration reached 11.2% and began to fall with further passage of air. The mixture was then heated to 110° and oxidation continued at this temperature until the hydroperoxide disappeared completely from the mixture, i.e., 125 hr. The reaction mixture (132 g) was treated with 10% aqueous NaOH solution to extract acid products; the alkaline layer was separated from the neutral one and the latter washed with water, dried with $MgSO_4$, and distilled. This yielded 83 g (62.9%) of unoxidized (I), 20.4 g (16.1%) of (IV), and 0.13 g (about 1%) of (VI). Treatment of the alkaline layer with concentrated hydrochloric acid liberated 5.04 g or 3.4% of (V) and 1.85 g of tar.

In the autooxidation of 128 g of (I) in the presence of 1 mg of manganese resinate, 500 mg of sodium stearate, 150 mg of cobalt acetate, 120 mg of NaOH, and 300 mg of calcium hydroxide, the maximum hydroperoxide content of 3.1% was reached after 16 hr. With further passage of air, the hydroperoxide concentration began to fall and no hydroperoxide was detected in the reaction mixture after 47 hr. After air had been passed for 133 hr, the weight of the reaction mixture was 133.5 g and treatment of this mixture as described above yielded 13.7 g (10.3%) of unoxidized (I), 96.29 g (74.5%) of (IV), 10.6 (8.3%) of (VI), 1.3 g (about 1%) of (VII), and 2 g of tar.

Data from experiments on the autooxidation of (I) up to the formation of the maximum hydroperoxide concentration in the reaction mixture are given in the table.

A reaction mixture contining 21.7% of p-ethylisopropylbenzene hydroperoxide had d_4^{20} 0.9841, n_D^{20} 1.5040.

Sulfuric acid cleavage of p-ethyl-sec-butylbenzene hydroperoxide. A 79.8-g sample of reaction mixture containing 12.6% of hydroperoxide was placed in a three-necked flask with a stirrer, reflux condenser, thermometer, and dropping funnel and with vigorous stirring at room temperature and then at 70–80°, 10% sulfuric acid was added dropwise until a reaction for hydroperoxide was negative (6 ml of sulfuric acid was added over 66 hr). After decompositon of the reaction product the mixture was treated repeatedly with small portions of 10% sodium hydroxide solution until the acid products had been extracted completely, the alkaline solution treated with ether, the ether extract added to the hydrocarbon layer, the alkaline solution mixed with concentrated hydrochloric acid to a weakly acid reaction, and the products were extracted with ether, washed with water, dried with magnesium

sulfate, and distilled. This yielded 49.93 g (62.5%) of unoxidized (I), 14.22 g (17.6%) of (IV), 3.43 g (4.3%) of (V), and 4.2 g of tar.

Autooxidation of p-sec-butylacetophenone. A mixture of 33 g of p-sec-butylacetophenone (IV), which was obtained by oxidation of (I) (b.p. 125–129° at 7 mm, d_4^{20} 0.9750, n_D^{20} 1.5190), 0.2 mg of manganese resinate, 30 mg of cobalt acetate, 100 mg of sodium stearate, 60 mg of calcium hydroxide, and 20 mg of sodium hydroxide was oxidized with atmospheric oxygen. After 43 hr, the mixture began to deposit crystals on standing. The oxidation was continued for 96 hr. Hydroperoxide was absent from the reaction mixture from the beginning to the end of the process and this is probably explained by the ready decomposition of the hydroperoxide of (IV) under the given conditions. Appropriate treatment of the reaction products yielded 15.2 g (46.6%) of p-diacetylbenzene and 17.6 g of unoxidized (IV).

Characteristics of oxidation products of p-ethyl-sec-butylbenzene

p-Sec-butylphenol is a colorless liquid. It has b.p. 67–77° (2 mm), d_4^{20} 1.1020, n_D^{20} 1.5230. On standing, it crystallized in white needles. The m.p. was 52–54° (from aqueous alcohol). Literature data [13]: m. p. 59°. A mixed melting point with p-sec-butylphenol, obtained by alkylation of phenol with pseudobutylene in the presence of $BF_3 \cdot H_3PO_4$, was not depressed.

Materials for autooxidation (mg)				Maximum hydroperoxide concentration (%)	Time to reach maximum hydroperoxide concentration (hr)	Final hydroperoxide concentration (%)
p-ethyl-sec-butylbenzene	manganese resinate	sodium hydroxide	other additives			
35.0	0.65	–	–	5.5	27	5.2
36.7	0.67	47	–	16.3	80	15.3
30.0	0.50	60	CH_3OH (1 ml)	18.4	64	16.1
30.0	0.60	400	–	15.0	81	13.4
94.7	1.00	50	Hydroperoxide of (I) (1.42 g)	14.9	72	12.6
33.7	2.10	–	$Ca(OH)_2$ (208 mg)	21.7	29	18.5

p-Acetylbenzoic acid formed a finely crystalline, white powder. The m.p. was 203–204° (sublimation and recrystallization from alcohol); its methyl ester had m.p. 89.5–90°. Literature data [14]: for the acid, m.p. 208°, for the methyl ester, m.p. 92°.

p-sec-Butylacetophenone is a colorless liquid with a weak, pleasant odor. It had b.p. 125–129° (7 mm), d^{20}_4 0.9750, n_D^{20} 1.5190. MR_D 54.76; Calc. 54.03. The 2,4-dinitrophenylhydrazone formed orange scales. It had m.p. 145–146°. Literature data [15]: for the ketone, b.p. 130–131° (7–8 mm), n_D^{20} 1.5182; for the 2,4-dinitrophenylhydrazone, m.p. 146–147°.

p-Diacetylbenzene formed white scales. The m.p. was 113–113.5° (from alcohol). A mixed melting point with p-diacetylbenzene, obtained by oxidation of p-ethylacetophenone [16], was not depressed. Literature data [16]: m.p. 113-114°.

SUMMARY

1. A study was made of the autooxidation of p-ethyl-sec-butylbenzene and p-sec-butylacetophenone with atmospheric oxygen in the presence of manganese resinate, sodium hydroxide, and other additives at 110°.

2. It was shown that despite the presence of a tertiary alpha C atom in the butyl radical in p-ethyl-sec-butylbenzene, the attack of molecular oxygen was largely directed at the alpha C atom of the ethyl radical, resulting in the formation of α-methyl-p-sec-butylbenzyl hydroperoxide; the main reaction product from prolonged oxidation was therefore p-sec-butylacetophenone.

3. It was found that p-sec-butylacetophenone may be oxidized to p-diacetylbenzene by atmospheric oxygen in 47% yield.

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REACTIONS OF NITROGEN OXIDES WITH POLYFLUORINATED ETHYLENES

PREPARATION AND REDUCTION OF POLYFLUORINATED NITROSO COMPOUNDS

V. A. Ginsburg, N. F. Privezentseva, N. P. Rodionova, S. S. Dubov, S. P. Makarov, and A. Ya. Yakubovich

Translated from Zhurnal Obshchei Khimii, Vol 30, No. 7, pp. 2406-2409, July, 1960
Original article submitted June 4, 1959

One of us showed previously [1] that nitrosyl chloride adds readily to the double bond of chlorinated olefins to form the corresponding chloronitroalkanes or their conversion products. This reaction was later extended to fluorinated ethylenes [2, 3] and in this case there were formed the corresponding chloronitro derivatives or acid halides of hydroxamic acids, if there was a hydrogen atom at the carbon atom forming the C–N bond. Haszeldine showed that nitrosyl bromide and also nitryl chloride add to halogenated ethylenes analogously [3]. The addition of nitrogen dioxide to polyfluorinated ethylenes forms the corresponding dinitroalkanes [4, 5]. Knunyants and Fokin, who made a detailed study of the nitration of perfluoroolefins, found [6, 7] that at room temperature, nitrogen dioxide converts an olefin into the corresponding dinitroalkane and nitronitrite, while at temperatures above 100°, the reaction is more complex, giving a series of products including nitrosoalkanes.

It seemed interesting to study the behavior of polyfluorinated ethylenes toward N_2O_3. In this case, the reaction could lead to the corresponding nitronitroso compounds as occurs with nonfluorinated unsaturated compounds.

The gas-phase reaction of N_2O_3 with tetrafluoroethylene, even at room temperature, readily formed an intense blue liquid, which was 2-nitro-1,1,2,2-tetrafluoronitrosoethane (cf. [6, 7]). Together with this main reaction product (more than 60% yield), the dinitro derivative of tetrafluoroethylene and a small amount of unidentified high-boiling substances were formed. Analogously, N_2O_3 and trifluoroethylene formed a chlorine-containing nitronitroso compound.

Like other polyfluorinated nitroso compounds described by Ruff,[8], Huckel [9], and then Haszeldine [3], the nitronitroso compounds obtained were comparatively stable and did not form dimers. The infrared spectrum of the nitroso compound obtained from tetrafluoroethylene showed the characteristic frequencies of the valence vibrations of N=O and C–N bonds at 6.2 and 12.25 μ, respectively, which practically coincided with the frequencies given for analogous compounds [10]. Reduction of perfluoronitronitrosoethane with hydriodic acid in ether gave the acid fluoride of nitrodifluoroacethydroxamic acid, which was isolated as the stable etherate. The structure of this substance was confirmed by the fact that its infrared spectrum contained the frequencies characteristic of an NO_2 group (6.29 μ) [11] and a C=N group (5.89 μ) [11-13]. The low frequency of the OH bond (3.15-3.20 μ) apparently indicated strong association of the substance. The analogous reaction of trifluorochloronitronitrosoethane formed the acid fluoride of the same hydroxamic acid. This conversion unequivocally demonstrates the structure of this compound as $NO_2CF_2CFClNO$. Evidently, the groupings $-CF_2NHOH$ and $-CFClNHOH$ in the intermediate products of the reduction described are unstable and tend to lose the elements of hydrogen halide and from our experiments it follows that the elimination of HCl proceeds more readily than that of HF.

$$NO_2CF_2CFXNO \longrightarrow [NO_2CF_2CFXNHOH] \xrightarrow{-HX} NO_2CF_2CF{=}NOH$$
where X = F, Cl.

A similar conversion was observed previously in the reduction of trichloronitrosomethane [14].

The structure of the nitronitroso compound obtained from N_2O_3 and trifluorochloroethylene shows that in the reaction examined, the addition of the elements of N_2O_3 proceeds in such a way that the nitroso group is attached to the carbon atom with the greatest electron density. This direction of addition does not correspond to the order of ionic addition; for the analogously directed addition of N_2O_3 to acrylic systems, Shechter and Ley proposed a homolytic mechanism [15]. It may be assumed that the NO_2 radical formed by dissociation of N_2O_3 begins the process, adding to the unsaturated system, and the nitroaliphatic radical thus formed then combines with NO. This hypothesis is confirmed to some extent by the fact that the olefins we studied themselves do not react with NO (in the dark). The reaction of gaseous mixtures of $CF_2=CF_2$ or $CF_2=CFCl$ with NO under irradiation leads to the corresponding nitronitroso compounds due to conversion of NO to N_2O_3 and addition of the latter to the olefin. It is interesting to emphasize the fact that in the reaction of N_2O_3 with trifluorochloroethylene, the NO_2 radical is directed to the CF_2 group of $CF_2=CFCl$, i.e., behaves similarly to other radicals investigated in the reaction with this olefin, such as Br and CF_3 [16, 17].

EXPERIMENTAL

1. Reaction of $CF_2=CF_2$ and N_2O_3. Preparation of 2-nitro-1,1,2,2 tetrafluoronitrosoethane. A 6.6-liter evacuated flask was charged with tetrafluoroethylene and N_2O_3 in a ratio of 1:1. The reaction was complete after 6 hr. We isolated 45 g of the nitronitroso compound (42% on tetrafluoroethylene).

B.p. 25°, d_{20}^{20} 1.513.

Found %: C 14.08, 13.86; N 14.70, 14.98; F 43.50, 43.23. M 176. $C_2O_3N_2F_4$. Calculated %: C 13.6; N 15.5; F 43.5. M 176.

From the high-boiling still residues, we isolated 8.7 g of tetrafluorodinitroethane with b.p. 58° [4].

2. Reduction of 2-nitro-1,1,2,2-tetrafluoronitrosoethane. Preparation of nitrodifluoroacethydroxamyl fluoride etherate. With stirring and cooling in ice and salt, 5 g of the nitroso compound was gradually added dropwise to a mixture of 8 g of hydriodic acid and 20 ml of ether. After 30 min, the reaction mixture was washed with a saturated solution of sodium hyposulfite, extracted with ether, and the ether extract dried over sodium sulfate and distilled. We obtained 2.2 g of substance.

B.p. 56° at 50 mm, d_{20}^{20} 1.350, n_D^{20} 1.3330.

Found %: C 24.42, 24.38; H 3.08, 3.27; N 15.4, 15.1; F 30.46, 30.21; OC_2H_5 11.50, 11.62. $C_2HO_3N_2F_3 \cdot \frac{1}{2}(C_2H_5)_2O$. Calculated %: C 24.6; H 3.07; N 14.8; F 29.2; OC_2H_5 11.5.*

3. Reaction of $CF_2=CF_2$ and NO in ultraviolet light. A 3.15-liter flask of heat-resistant glass was charged with tetrafluoroethylene and NO in a volume ratio of 1:2 and then the flask was irradiated for 40 hr with a PRK-2 mercury-quartz lamp at a distance of 30-50 cm from the flask. We obtained 2.5 g of nitronitroso compound with b.p. 25°. The yield on tetrafluoroethylene was 35%.

4. Reaction of $CF_2=CFCl$ and N_2O_3. Preparation of 2-nitro-1,2,2-trifluoro-1-chloronitrosoethane. A 13.15-liter evacuated flask was charged with $CF_2=CFCl$ and N_2O_3 in a ratio of 1:1. After 4 hr, the reaction product was pumped out and distilled. We obtained 26.5 g of nitronitroso compound (washed with water and H_2SO_4).

B.p. 57° (or 8° at 50 mm), d_{20}^{20} 1.557, n_D^{20} 1.3360.

Found %: C 12.11, 12.20; N 13.70, 13.63; F 29.20; Cl 18.3. M 203. $C_2O_3N_2F_3Cl$. Calculated %: C 12.4; N 14.5; F 29.6; Cl 18.4. M 192.7.

The yield of nitronitroso compound was 61% on the trifluorochloroethylene.

5. Reduction of 2-nitro-1,2,2-trifluoro-1-chloronitrosoethane. Reduction of 5 g of 2-nitro-1,2,2-trifluoro-1-chloronitrosoethane with 8 g of hydriodic acid in ether by the procedure described above yielded 2.7 g of nitrodifluoroacethydroxamyl fluoride ethers.

B.p. 57° at 50 mm, d_{20}^{20} 1.351, n_D^{20} 1.3335.

Found %: C 23.37, 23.49; H 2.83, 2.60; N 14.31, 14.59; F 29.03, 29.06; OC_2H_5 11.97, 12.25. $C_2HO_3N_2F_3 \cdot \frac{1}{2}(C_2H_5)_2O$. Calculated %: C 24.6; H 3.0; N 14.4; F 29.3; OC_2H_5 11.5.

*Here and in analogous etherates, half of the alkoxyl groups present were determined by the standard Zeisel procedure.

SUMMARY

1. It was shown that the reaction of polyfluorinated olefins such as tetrafluoroethylene and trifluorochloroethylene with N_2O_3 in the gas phase forms polyfluorinated nitronitroso compounds. In the case of trifluorochloroethylene, the nitroso group is attached to the CFCl group of the olefin.

The same nitroso compounds are formed by the reaction of tetrafluoroethylene or trifluorochloroethylene with nitric oxide under ultraviolet irradiation.

2. Reduction of the nitronitroso compounds obtained with hydriodic acid leads to the formation of the acid fluoride of nitrodifluoroacethydroxamic acid, which was isolated as the etherate.

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REACTIONS OF HALOGENS, NITRIC OXIDE, AND POLYFLUORINATED ETHYLENES IN ULTRAVIOLET LIGHT

PREPARATION AND THERMAL DECOMPOSITION OF POLYFLUORINATED ALIPHATIC NITROSO COMPOUNDS

V. A. Ginsburg, N. F. Privezentseva, V. A. Shpanskii,
N. P. Rodionova, S. S. Dubov, A. M. Khokhlova,
S. P. Makarov, and A. Ya. Yakubovich

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2409-2415, July, 1960
Original article submitted June 4, 1959

In previous work, we showed [1] that the reaction of N_2O_3 with tetrafluoro- and trifluorochloroethylenes in the gas phase forms polyfluorinated nitronitroso compounds. This obviously radical reaction begins with the addition of an NO_2 radical to the olefin with subsequent combination of the nitroalkyl radical formed with NO. It seemed interesting to carry out the analogous reaction with polyfluorinated ethylene, NO, and halogen in ultraviolet light. It might have been conjectured that atomic chlorine or bromine would initiate a chain which would lead to the formation of the corresponding β-halodinitroso compounds.

Attempts to prepare such nitrosoalkanes by the reaction of nitrosyl chloride or bromide with polyhalogenated olefins were made previously by Yakubovich et al. [2, 3] and also by Haszeldine [4]; however, in all the cases described, no nitroso compounds were formed and the reaction products were the corresponding β-halonitro compounds or acid halides of hydroxamic acids. Nonetheless, it was suggested that nitroso compounds were formed as intermediate products in these reactions.

In actual fact, as is described below, it was shown later that the reaction of nitrosyl chloride with difluorodichloroethylene gives a satisfactory yield of 1,2-difluoro-1,2,2-trichloronitrosoethane, which was found to be quite stable under the experimental conditions and was isolated in a discrete state (see table, compound 6). It might have been conjectured that when the reaction was carried out in the gas phase (low concentrations), the oxidation of the nitroso compounds formed would be retarded and hence they would remain in the reaction sphere. Experiments confirmed this. In all cases, irradiation of mixtures of the gases $NO + Cl_2$ or $NO + Br_2$ with polyfluorinated ethylenes such as tetrafluoro-, trifluorochloro-, and trifluoroethylene in a ratio of olefin: NO: $Hal_2 = 1:1:\frac{1}{2}$ gave satisfactory yields of the corresponding nitroalkanes (see table), demonstrations of whose structures are given below.

These compounds were intense blue liquids, which were comparatively stable under normal conditions.

Together with nitroso compounds, from the reaction mixture we always isolated the corresponding alkene dihalides and, in a number of experiments, β-halonitro compounds, which were evidently obtained by partial oxidation of the nitroso compounds.

In the infrared spectra of the nitroso compounds described, the frequency of the N=O group vibrations was in the region 6.2-6.3 μ and, as a rule, changed very little. The structure of the β-halonitroso compounds obtained from the unsymmetrical olefin, trifluorochloroethylene (compounds 2 and 4), was established by reduction with

hydriodic acid. The intermediate polyfluoroalkylhydroxylamines thus formed were found to be unstable and, in accordance with the reactions we described in the previous communication [1], were converted into acid fluorides of polyfluoroacethydroxamic acids (isolated as etherates).

$$ClCF_2CFXNO \longrightarrow [ClCF_2CFXNHOH] \xrightarrow{-HX} ClCF_2CF{=}NOH$$
(Br)

where X = F, Cl.

The presence of the oxime grouping in the reduction product of 1,2,2-trifluoro-1,2-dichloronitrosoethane was confirmed by the infrared spectrum, which showed frequencies of the groups C = N (5.95 μ) and OH (3.15 μ), analogous to the corresponding frequencies for nitrodifluoroacethydroxamyl fluoride etherate [1]. The mass spectrum • of this substance showed the ions $HONCFCF_2^+$ (m/e 112, 24%), $CFCl^+$ (m/e 85 and 87, total intensity 4.5%), $NCFCF_2Cl^+$ (m/e 130, 2.79%), $HONCFCF_2Cl^+$ (m/e 128, 1.57%). In addition, the mass spectrum showed molecular ions of difluorochloroacethydroxamyl fluoride $HONCFCF_2Cl^+$ (m/e 147, 2.18%) and ether $C_4H_{10}O^+$ (m/e 74, 23.6%) and also ions derived from ether $C_3H_7O^+$ (m/e 59, 43.1%) and $C_2H_5O^+$ (m/e 45, 29.6%), which indicates the complex nature of the bond of the acid fluoride with ether in the compound studied. The ion with the maximum intensity in the spectrogram was one with m/e 31, 100%, which could be NOH^+ or CF^+.

The observed orientation in the addition of the elements of nitrosyl halide to the unsymmetrical olefin could be explained by an ionic mechanism in which the halide anion is added to the carbon atom with the least electron density. This scheme was demonstrated previously for the reaction of nitrosyl halides with fluoroolefins in the liquid phase [3].

$$\overset{\delta(+)}{CF_2}{=}\overset{\delta(-)}{CFCl} + \overset{\delta(+)}{NO}\overset{\delta(-)}{X} \longrightarrow CF_2NCFClNO,$$

Sample No.	Compound	Boiling point (pressure in mm)	d_0^{20}	n_D^{20}
1	CF_2ClCF_2NO	−5°	—	—
2	$CF_2ClCFClNO$	+36	2.042	1.3440
3	CF_2BrCF_2NO	+18	1.863	—
4	$CF_2BrCFClNO$	+10.5 (100)	1.665	1.3634
5	$CF_2ClCFHNO$	+40 (732)	—	—
6	$CFCl_2CFClNO$	81.5	1.575	1.3975

However, this mechanism did not occur in the gas reactions described. In actual fact, nitroso compounds were not formed even after prolonged contact (10 days) in a gaseous mixture of tetrafluoroethylene, NO, and Cl_2 in the dark at room temperature, even though nitrosyl chloride was obtained in a considerable amount. These observations indicate that under the conditions studied, the reaction of NO, halogen, and polyfluoroethylene proceeds by a radical mechanism with the reaction begun by atomic chlorine formed by the action of ultraviolet light. The chloroalkyl radical thus formed combines with NO to give the nitroso compound.

In mechanism, the reaction described is similar to the reaction of N_2O_3 with fluoolefins and in nature, it is close to the formation of nitrosocyclohexane from NO, Cl_2, and cyclohexane in ultraviolet light [5].

When reduced with hydriodic acid, nitroso compound 5 (table) was converted into the chlorine- and fluorine-containing ethylhydroxylamine $CF_2ClCFHNHOH$, which was also isolated as the etherate. Thus, this nitroso compound may be assigned the formula $CF_2ClCFHNO$, though the absence of a tendency to rearrange into the isonitroso form, which is normal for nitroso compounds with a α-hydrogen atom, has no analogy.

It seemed interesting to investigate the behavior of these nitroso compounds at high temperatures. For this purpose, 1,1,2,3-tetrafluoro-2-chloronitrosoethane and 2-nitro-1,1,2,2-tetrafluoronitrosoethane, which was described in the previous work, were heated in a steel tube under pressure to 120-130°. In both cases the decomposition products were found to contain the corresponding nitro derivatives $ClCF_2CF_2NO_2$ and $NO_2CF_2CF_2NO_2$ and also the polyfluorinated imines $ClCF_2CF_2N = CFCF_2Cl$ (I) and $NO_2CF_2CF_2N = CFCF_2NO_2$ (II). The structures of the latter

• The mass spectra were obtained on an MS-2 spectrometer with an electron energy of 40 ev.

were established from the analysis data and infrared spectra. Thus, together with the frequencies of the NO_2 group, (6.29 μ) the pyrolysis product of perfluoronitronitrosoethane (II) showed an intense band characteristic of the C= = N bond (5.66 μ). Thus, the thermal decomposition of the polyfluorinated nitrosoethanes described proceeds analogously to the decomposition of trichloronitrosomethane, which forms CCl_3NO_2 and $CCl_3N=CCl_2$ [6].

The mechanism of this conversion may be represented by a scheme of radical processes, beginning with decomposition of the nitroso compound at the C–NO bond and the addition of the polyfluoroalkyl radical to a neighboring nitroso molecule. The radical of the dialkyloxy nitrogen type formed then decomposes in the reducing medium created by the excess nitroso compound and metal walls of the vessel similarly to the homolytic decomposition of perfluoroalkoxyl radicals or perfluoroalkyl radicals in the presence of nitrogen oxides [7, 8].

$$R_fCF_2NO \longrightarrow R_fCF_2\cdot + NO$$
$$R_fCF_2NO + R_fCF_2\cdot \longrightarrow [(R_fCF_2)_2NO\cdot] \longrightarrow R_fCF_2N(OF)=CFR_f]$$
$$R_fCF_2NO \rightarrow R_fCF_2NCF_2R_f + R_fCF_2NO_2 + F.$$

In this connection, the mass spectra of the nitroso compounds studied are interesting. The most intense ion in them was NO^+ (m/e 30, 100%). This indicates that the decomposition of these nitroso compounds actually proceeds most readily at the C–NO bond, which is the weakest. Other intense ions in the spectra were $C_2F_2N^+$ (m/e 76, 30%), $C_2F_4^+$ (m/e 100, 19%), $C_2F_4Cl^+$ (m/e 135, 18.7%) for $ClCF_2CF_2NO$ and $C_2F_4^+$ (m/e 100, 24.2%), NO_2^+ (m/e 46, 16.9%) and $C_2F_2N^+$ (m/e 76, 12%) for $NO_2CF_2CF_2NO$. The data presented agree to a certain extent with the mechanism proposed for the thermal decomposition of the nitroso compounds.

EXPERIMENTAL

1. Reaction of $CF_2=CF_2$, NO, and Cl_2 in ultraviolet light. Preparation of 1,1,2,2-tetrafluoro-2-chloronitrosoethane. An evacuated (residual pressure 1 mm) 13-liter round-bottomed flask of heat-resistant glass was charged with C_2F_4, NO, and Cl_2 in a ratio of 1:1:$\frac{1}{2}$ by volume and then the flask was irradiated with ultraviolet light (PRK-2 mercury-quartz lamp) at room temperature. The reaction was complete after 15-18 hr. The reaction products were pumped out into a trap, cooled with liquid air, and distilled on a column with an efficiency of 100 theoretical plates.

The low-boiling fractions were freed from nitrogen oxides by bubbling through water and conc. H_2SO_4. We collected 13.5 g of tetrafluorochloronitrosoethane with b.p. -5° (according to data in [4]: b.p. -2°). The yield of nitroso compound was 38% on C_2F_4.

Found %: C 14.9, 14.70; N 8.31, 8.59; F 45.30, 46.25; Cl 21.66, 22.40. M 171.0. C_2ONClF_4. Calculated %: C 14.50; N 8.46; F 45.8; Cl 21.4. M 165.5.

Together with this substance, from the reaction products we isolated 2.5 g of symmetrical tetrafluorodichloroethane with b.p. 3.5° (molecular weight 170.5) and 2-chloro-2,2,1,1-tetrafluoronitroethane with b.p. 34°.

2. Reaction of $CF_2=CF_2$, NO, and Cl_2 without irradiation. A 6.75-liter flask was charged with NO, Cl_2, and C_2F_4 in a ratio of 1:$\frac{1}{2}$:1 and then the flask was kept in the dark for 10 days. The products were pumped out and distilled on a column. Fractions were collected: 9.8 g of product with b.p. 78-77° (molecular weight 101.0, tetrafluoroethylene) and 5.4 g of nitrosoyl chloride with b.p. 10-5°, which appeared as a red-brown liquid that froze in carbon dioxide and was hydrolyzed completely by water.

3. Pyrolysis of 1,1,2,2-tetrafluoro-1-chloronitrosoethane. A 6.5-g sample of $ClCF_2CF_2NO$ was heated at 120-130° for 4 hr in a 75-ml metal tube and then the products were pumped out into a trap, cooled with liquid air, and fractionated repeatedly. We isolated 2.2 g (42%) of a fraction with b.p. 75°.

d_{20}^{20} 1.621, n_D^{20} 1.3200.

Found %: C 17.47, 17.94; N 5.41, 5.35; F 50.95, 51.0; Cl 25.87, 24.02. M 278. $ClCF_2CF_2N=CFCF_2Cl$. Calculated %: C 18.06; N 5.28; F 50.02; Cl 26.6. M 266.

Together with this fraction, the reaction mixture yielded 1.5 g of β-chloroperfluoronitrosoethane with b.p. 35-36°, which was identical with that described in [4].

4. Pyrolysis of 2-nitro-1,1,2,2-tetrafluoronitrosoethane. A 10-g sample of the nitronitroso compound was heated at 120-130° for 5 hr in a 40-ml steel tube.

Distillation of the reaction products yielded 5.5 g (50%) of tetrafluorodinitroethane with b.p. 55-59° (according to data in [4]: b.p. 57-59°) and 3 g of a substance with b.p. 52° at 50 mm.

d_{20}^{20} 1.719, n_D^{20} 1.3520.

Found %: C 17.01, 16.80; N 14.54, 14.33; F 45.08, 45.80. $NO_2CF_2CF_2N=CFCF_2NO_2$. Calculated %: C 16.73; N 14.6; F 46.4.

5. Reaction of NO, Cl_2, and $CF_2=CFCl$ in ultraviolet light. Preparation of 1,2,2-trifluoro-1,2-dichloronitrosoethane. A 13.15-liter flask of heat-resistant glass was charged with $CF_2=CFCl$, Cl_2, and NO in a ratio of $1:\frac{1}{2}:1$ and then the flask was irradiated with a PRK-2 mercury-quartz lamp for 40 hr. At the end of the reaction, the mixture was distilled. We collected 11 g (35%) of dichlorotrifluoronitrosoethane with b.p. 36° (-8° at 125 mm), which was freed from nitrogen oxides by bubbling through water and conc. H_2SO_4 in vacuum.

Found %: C 13.22, 13.30; F 31.40, 30.70; Cl 40.00, 40.07. M 184. $C_2ONCl_2F_3$. Calculated %: C 13.48; F 31.3; Cl 39.0 M 182.

Repeated distillation of the high-boiling fractions yielded 6.3 g of trichlorotrifluoroethane with b.p. 48°.

6. Reduction of 1,2,2-trifluoro-1,2-dichloronitrosoethane. Preparation of difluorochloroacethydroxamyl fluoride etherate. With stirring and cooling in a mixture of ice and salt, 5 g of trifluorodichloronitrosoethane was added dropwise to a mixture of 8 g of technical hydriodic acid and 25 ml of ether. After 30-45 min, the reaction mixture was treated with a saturated solution of sodium hyposulfite and extracted with ether; the ether extract was dried with baked sodium sulfate and vacuum distilled.

We isolated 2.2 g of difluorochloroacethydroxamyl fluoride etherate with b.p. 60° at 145 mm.

d_{20}^{20} 1.231, n_D^{20} 1.360

Found %: C 27.05; H 3.03; N 6.84; F 30.9; Cl 19.4. $C_2HONClF_3\cdot\frac{1}{2}(C_2H_5)_2O$. Calculated %: C 26.0; H 3.25; N 7.60; F 30.9; Cl 19.15.

7. Reaction of $CF_2=CF_2$, NO, and Br_2 in ultraviolet light. Preparation of 1,1,2,2-tetrafluoro-2-bromonitrosoethane. A mixture of $CF_2=CF_2$, NO, and Br_2 in a ratio of $1:1:\frac{1}{2}$ was irradiated in a 13-liter flask. After 15-20 hr, the products were pumped out and separated by fractionation. The nitroso compound was freed from nitrogen oxides by bubbling through water and conc. H_2SO_4 in vacuum. We obtained 17.5 g (40% on C_2F_4) of nitroso compound with b.p. 18°, which corresponds to literature data [4].

Found %: C 12.05, 12.74; N 7.01, 7.08; F 36.61, 36.67. M 185. C_2ONF_4Br. Calculated %: C 11.4; N 6.6; F 36.2. M 210.

The high-boiling residue yielded 11.8 g of dibromotetrafluoroethane with b.p. 46° and 40 g of β-bromotetrafluoronitroethane with b.p. 58° [4].

8. Reaction of $CF_2=CFCl$, NO, and Br_2 in ultraviolet light. Preparation of 1,2,2-trifluoro-1-chloro-2-bromo nitrosoethane. A mixture of $CF_2=CFCl$, NO, and Br_2 in a ratio of $1:1:\frac{1}{2}$ was irradiated in a 13-15-liter flask for 30.35 hr. Distillation of the reaction mixture yielded 3.5 g of nitroso compound with b.p. 10.5° at 100 mm.

Found %: C 9.25, 9.99; N 6.71, 6.52; F 23.9, 23.5. M 221.5. C_2ONF_3ClBr. Calculated %: C 10.6; N 6.18; F 25.15. M 226.5.

The high-boiling residue yielded 6.3 g of 1,2,2-trifluoro-1-chloro-1,2-dibromoethane with b.p. 96°.

9. Reduction of 1,2,2-trifluoro-1-chloro-2-bromonitrosoethane. Preparation of difluorobromoacethydroxamyl fluoride etherate. A 5-g sample of the nitroso compound was reduced with 8 g of hydriodic acid as in experiment 6. We obtained 2.5 g (46%) of difluorobromoacethydroxamyl fluoride etherate with b.p. 62.5° at 100 mm.

d_{20}^{20} 1.5217, n_D^{20} 1.3845

Found %: C 21.59, 21.32; H 2.89, 3.01; N 6.39, 6.57; F 23.48, 23.75; Br 34.89, 34.19; OC_2H_5 18.26. $C_2HONF_3Br\cdot\frac{1}{2}(C_2H_5)_2O$. Calculated %: C 20.95; H 2.62; N 6.12; F 24.83; Br 34.92; OC_2H_5 19.65.

10. Reaction of $CF_2=CFH$, NO, and Cl_2 in ultraviolet light. Preparation 1,2,2-trifluoro-2-chloronitrosoethane. A mixture of $CF_2=CFH$, NO, and Cl_2 in a ratio of $1:1:\frac{1}{2}$ in a 13-15-liter flask was irradiated for 50 hr

with a PRK-2 mercury-quartz lamp and then the reaction mixture was pumped out and distilled on a column with an efficiency of 100 theoretical plates. We isolated 4.8 g of nitroso compound with b.p. 10° at 432 mm.

Found %: C 16.53, 16.60; H 1.13, 1.26; N 9.83, 9.74; F 38.2; Cl 23.6. C_2NONF_3Cl. Calculated %: C 16.27; H 0.67; N 9.50; F 38.6; Cl 24.1.

11. Reduction of 1,2,2-trifluoro-2-chloronitrosoethane with hydriodic acid. A 5.0-g sample of the nitroso compound was reduced by the procedure described above. We obtained 0.8 g of product with b.p. 36-38° at 50 mm.

d_{20}^{20} 1.3504, n_D^{20} 1.3735.

Found %: C 25.70, 25.24; H 3.83, 3.30; N 7.70, 7.89; F 29.94; Cl 20.79; OC_2H_5 13.28. $C_2H_5ONF_3Cl \cdot \frac{1}{2}(C_2H_5)_2O$. Calculated %: C 26.0; H 4.35; N 7.6; F 30.9; Cl 19.2; OC_2H_5 12.2.

12. Reaction of symm-difluorodichloroethylene with nitrosyl chloride in the liquid phase. Preparation of 1,2-difluoro-1,2,2-trichloronitrosoethane. A mixture of 35 g of nitrosyl chloride and 75 g of symm-dichlorodifluoroethylene was kept at room temperature in two glass ampoules for 8 days. Distillation of the reaction products yielded 13 g of dark blue liquid with b.p. 81.5°.

Found %: C 13.23, 13.22; F 18.97; M 187.4. $C_2ONF_2Cl_3$. Calculated %: C 12.09; F 19.15. M 198.4.

SUMMARY

1. It was shown that the reaction of polyfluorinated olefins such as tetrafluoro-, trifluorochloro-, and trifluoroethylene with a mixture of $NO+Cl_2$ or $NO+Br_2$ in the gas phase under irradiation from a mercury-quartz lamp forms the corresponding β-chloro (or bromo) nitrosoalkanes. No reaction occurs without irradiation.

2. Reduction of the nitroso compounds obtained from trifluorochloroethylene yielded the corresponding chlorodifluoro- and bromodifluoroacethydroxamyl fluorides, which indicated addition of the halogen in the reaction of NO, Hal_2, and olefin to the CF_2 group of the latter.

3. Pyrolysis of the nitroso compounds $ClCF_2CF_2NO$ and $NO_2CF_2CF_2NO$ at 120-130° yielded the polyfluorinated ethylenimines $ClCF_2CF_2N = CFCF_2Cl$ and $NO_2CF_2CF_2N = CFCF_2NO_2$, respectively.

4. The infrared and mass spectroscopic characteristics of the nitroso compounds obtained are given.

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POLAROGRAPHIC INVESTIGATION OF GLYOXYLIC ACID

V. S. Bezuglyi, V. N. Dmitrieva, T. S. Tarasyuk,

and N. A. Izmailov

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2415-2421,
July, 1960
Original article submitted April 5, 1959

We know of only two papers on the reduction of glyoxylic acid. In one of them [1], it was only reported that glyoxylic acid is reduced on a mercury dropping electrode and no concrete data on the nature of the reduction, half-wave potential, etc. were given. The second paper [2] was mainly devoted to the reduction of oxalic acid on a mercury dropping electrode. It also contained some data on a polarographic investigation of glyoxylic acid in a base electrolyte of KCl with HCl and KOH added. In particular, it was shown that in acid solutions (KCl+HCl), $E_{\frac{1}{2}}$ of glyoxylic acid changes with a change in pH and a second wave appears at pH 4.3, for which $E_{\frac{1}{2}}$ = 1.320 relative to a normal calomel electrode, and the first wave disappears. Among other derivatives similar to glyoxylic acid, only phenylglyoxylic acid has been studied polarographically [3].

EXPERIMENTAL

Glyoxylic acid was prepared by electrolytic reduction of oxalic acid*.

Oxalic acid is normally reduced to glyoxylic acid on a lead-silver or mercury cathode in the presence of sulfuric acid. This method has been described in the literature [4]. However, the mercury electrode may be replaced by a lead electrode. The anode may be the lead vessel itself (1.5 liter), which is charged with a mixture of acids (50 g of oxalic acid and 50 g/liter of sulfuric acid). The anode space was separated from the cathode space by a porous fireclay diaphragm. The cathode was a lead plate, immersed in 5% H_2SO_4 solution. The reduction of oxalic acid was carried out for 10 hr at a current strength of 5 amp and a potential of 5 v. Reduction under these conditions normally yielded a glyoxylic acid solution with an average strength of 3%.

In the electrolytic preparation, the electrolyte may contain oxalic, sulfuric, and glycolic acids in addition to glyoxylic acid. Glycolic acid is formed by further reduction of glyoxylic acid. Attempts to isolate glyoxylic acid from this mixture of acids by the procedure described in the literature [5] were unsuccessful as glyoxylic acid and its salts decomposed on heating to form glycolic and oxalic acids or their salts [6]. As a result, we modified this method.

The mixture of acids obtained was treated with excess calcium carbonate. Only calcium glyoxylate remained in solution. The solution obtained was filtered through paper to remove the precipitate of calcium salts and an equal amount of alcohol added to it to precipitate calcium glyoxylate. This salt was recrystallized repeatedly from alcohol and dissolved in water. For isolation of free glyoxylic acid, the solution obtained was passed through an ion-exchange column with cationite, 500 mm high and 10 mm in diameter; the solution flowed from the column at 0.3 ml per min. The cationite used was espatit in the H form. The acid was collected in fractions and each fraction was checked to ensure that calcium ions and traces of other acids (sulfuric and oxalic) were absent. The fractions were combined.

The glyoxylic acid solution obtained gave characteristic reactions for an aldehyde group (with Schiff's reagent and also an aqueous solution of indole) and an acid (action on an indicator).

* The authors are very grateful to V. P. Polyakov for providing the means of preparing glyoxylic acid.

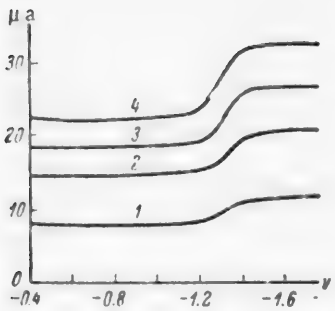


Fig. 1. Polarograms of glyoxylic acid in a base electrolyte of 0.05 N $(C_2H_5)_4NOH$. Glyoxylic acid concentration (mole/liter): 1) 1.12, 2) 2.19, 3) 3.22, 4) 4.22.

The concentration of purified glyoxylic acid was determined iodometrically [7] and equalled 0.1075 M.

Polarographic investigation of glyoxylic acid

The polarographic measurements were made with an FG-8 polarograph with a mercury dropping electrode that had the following characteristics: m = 0.954 mg/sec, τ = 5.5 sec (at E = 0), $m^{2/3} \cdot \tau^{1/6} = 1.237$ $mg^{2/3}$ $sec^{1/2}$. The galvanometer sensitivity was $3 \cdot 10^{-9}$ amp.

The base electrolytes for polarography were 1 N $MgCl_2$, 0.05 N $(C_2H_5)_4NOH$, and buffer solutions, which were prepared by the method described by Britton [8].

In the acid region, we used Walpole's buffer solutions, in the medium pH region, Kolthoff and Palich's buffer solutions, and in the alkaline region, Sorensen, Kolthoff, and Ringer's buffer solutions. In addition, we repeated the experiments of

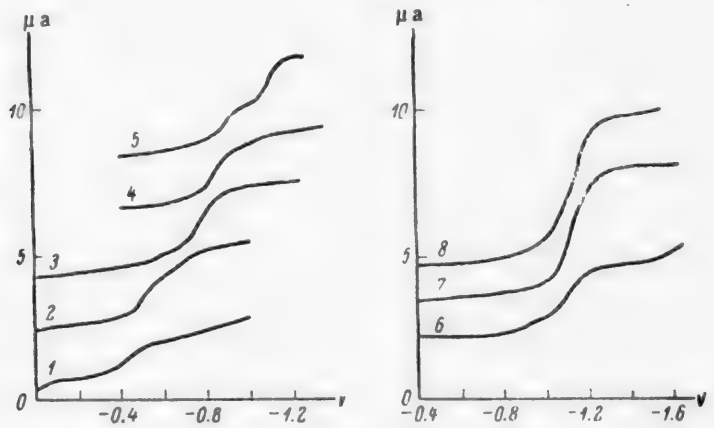


Fig. 2. Polarograms of glyoxylic acid (c = 18 mmole/liter) in base electrolytes of buffer solutions with different pH values. pH values: 1) 2.05, 2) 3.75, 3) 4.65, 4) 5.75, 5) 6.65, 6) 7.2, 7) 7.9, 8) 8.3.

G. M. Florianovich [2] in solutions of KCl+HCl (+KOH). The half-wave potentials were measured against a saturated calomel electrode. As the polarographic results showed, glyoxylic acid is reduced on a mercury dropping electrode in a base electrolyte of 0.05 N $(C_2H_5)_4NOH$ and in buffer mixtures with various pH values.

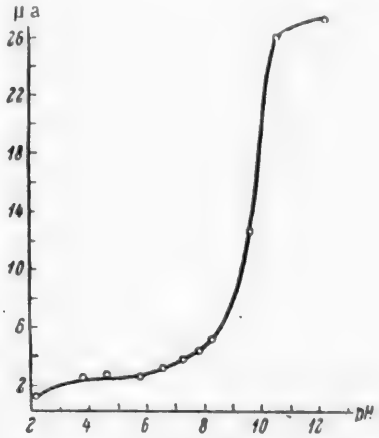


Fig. 3. pH dependence of the limiting current (I_d) of glyoxylic acid.

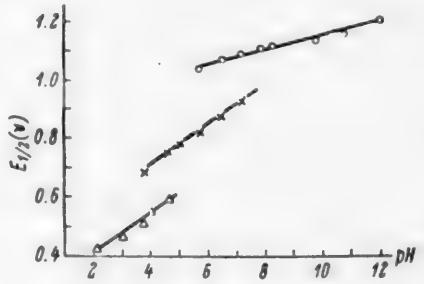


Fig. 4. pH dependence of the half-wave potentials ($E_{\frac{1}{2}}$) of glyoxylic acid.

Figure 1 gives curves obtained in the study of glyoxylic acid solutions in a base electrolyte of 0.05 N $(C_2H_5)_4NOH$ and Fig. 2, in base electrolytes of buffer solutions. As these figures

show, at a glyoxylic acid concentration of 0.018 M, a galvanometer sensitivity of 1/50, and 20°, polarographic waves of glyoxylic acid were observed and these were particularly well expressed in alkaline solutions.

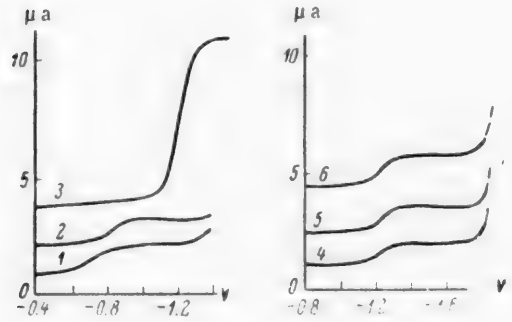


Fig. 5. Polarograms of glyoxylic acid in a base electrolyte of 0.1 N KCl with additions of 0.1 N HCl and 0.1 N KOH. Glyoxylic acid concentration c = 4.4 mmole/liter: 1) without HCl added (pH 6.6); 2) 0.07 ml HCl (pH 4.9); 3) 0.2 ml HCl (pH 3.9). Glyoxylic acid concentration c = 0.88 mmole/liter: 4) without KOH added; 5) 0.06 ml KOH; 6) 0.22 ml KOH.

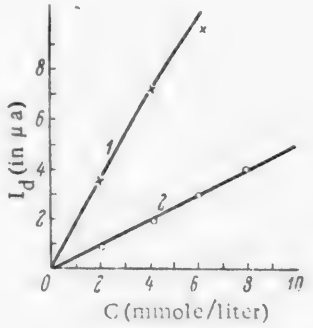


Fig. 6. Calibration lines of glyoxylic acid in a base electrolyte of buffer solutions. 1) pH 12, 17°, 2) pH 3.95, 38°.

At lower glyoxylic acid concentrations in acid and neutral solutions, a diffusion current of glyoxylic acid reduction did not appear on the polarograms.

Figure 3 shows the change in the limiting current of glyoxylic acid reduction with a change in solution pH.

One wave was observed (at pH 2.05, $E_{\frac{1}{2}}$ = -0.42 v) in strongly acid buffer solutions. A second wave appeared, beginning with pH 3.5 (at pH 3.75, $E^1_{\frac{1}{2}}$ = -0.52v and $E^2_{\frac{1}{2}}$ = -0.70 v). With a further increase in pH, both waves were retained up to pH 5.75, when the height of the first wave gradually fell and at pH 5.75, this wave disappeared completely, while the height of the second wave increased. At pH 5.7, a third wave appeared ($E^3_{\frac{1}{2}}$ = - 1.05 v) with the gradual disappearance of the second. At pH 7.2, the second wave disappeared completely and there remained only one wave, whose $E_{\frac{1}{2}}$ value changed little with a change in the pH of the buffer solution (at pH 7.9, $E^3_{\frac{1}{2}}$ = = -1.12 v and at pH 12, $E_{\frac{1}{2}}$ = -1.22 v).

Figure 4 gives the pH dependence of $E_{\frac{1}{2}}$ of glyoxylic acid.

The nature of the change in the polarographic waves in a solution of KCl + HCl (or + KOH) is presented in Fig. 5, which shows that these results are close to those obtained in [2].

As has been pointed out already, the height of the polarographic waves of glyoxylic acid depends strongly on pH and temperature.

Figure 6 gives the relation between the diffusion current and the glyoxylic acid concentration at various base electrolyte pH values and at various temperatures. As this figure shows, the slope of the calibration line at high pH values is higher than at low values.

Figure 7 gives the relation of log I_d to 1/T for different polarographic conditions and this is represented by straight lines with different slopes, depending on the pH of the base electrolyte.

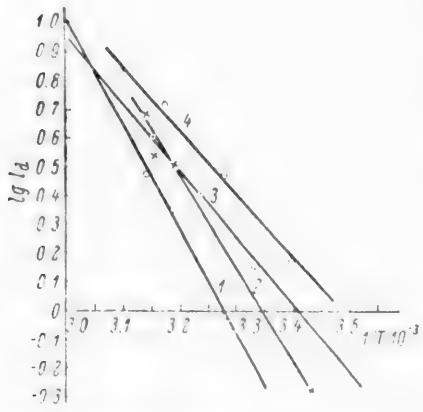


Fig. 7. Relation of log I_d to 1/T. pH values: 1) 3.7, 2) 6.7, 3) 9.42, 4) 10.7.

RESULTS

As the experimental data presented show, the carbonyl group in glyoxylic acid is reduced at more positive potentials than in the case of aliphatic aldehydes and this is connected with the lower electron density at the

carbonyl group of glyoxylic acid due to its conjugation with the electronegative CO group of the carboxyl.

As a result of this, the positive charge of the carbonyl carbon atom in the glyoxylic acid molecule is somewhat greater than with other aldehydes (in the latter, the positive induction effect of the alkyl groups reduces the positive charge); therefore, even such a weak nucleophilic reagent as water can react readily with the carbonyl group of glyoxylic acid.

In actual fact, there are reports in the literature that glyoxylic acid is hydrated (bound to one water molecule) in aqueous solution [2] and in this connection, it has been assigned the structure of dihydroxyacetic acid $CH(OH)_2COOH$.

This state of glyoxylic acid in aqueous solution has a corresponding effect on its polarographic behavior at a dropping mercury cathode. There is:a) a very low diffusion current (the value of n, i.e., the number of electrons involved in the reduction of one glyoxylic acid molecule, calculated from the Ilkovic equation, is very small); b) a strong temperature dependence of the wave height; c) an increase in the wave height in alkaline solutions.

These phenomena are explained by the fact that as in other cases (formaldehyde [10-13], monochloroacetaldehyde [14], etc.), in an aqueous solution of glyoxylic acid there is an equilibrium between its hydrate and aldehyde forms. The unhydrated molecules, of which there are very few in acid, neutral, and weakly alkaline solutions at normal temperature, undergo reduction. With a rise in temperature, the equilibrium is displaced toward the unhydrated form, there is an increase in the number of unhydrated glyoxylic acid molecules undergoing reduction, and the limiting current on the polarograms increases. Thus, the current has a kinetic character and may be represented by the equation

$$I_d = K_1 e^{-\frac{Q}{RT}} \quad \text{or} \quad \lg I_d = A - \frac{Q}{2.3R} \cdot \frac{1}{T},$$

in which Q is the activation energy of the given reaction.

As this equation shows, there should be a linear relation between $\log I_d$ and $1/T$ and as Fig. 7 shows, this is actually the case. From the slopes of the lines in the coordinates $\log I_d - 1/T$ for various pH values, we determined the activation energy of dehydration of glyoxylic acid molecules. The results of these determinations are given in the table.

Activation Energies Q of Glyoxylic Acid Dehydration at Various pH Values

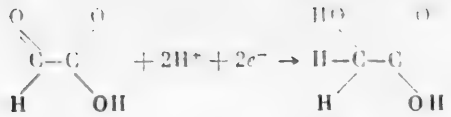
pH	3.7	6.7	9.42	10.7
Q (kcal/mole)	16900	14800	10700	10500

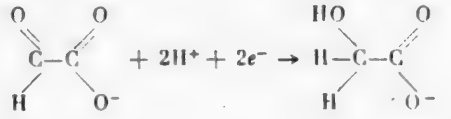
The fall in the activation energy with a change to an alkaline solution is apparently connected, on the one hand, with a substantial change in the state of the glyoxylic acid molecules, namely, with their complete ionization, which substantially affects the electronic state of the separate groups.

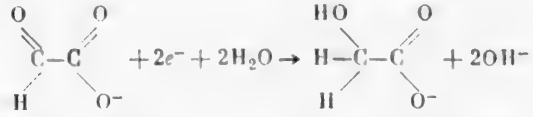
The appearance of an effective negative charge on one of the oxygens of the carboxyl group leads to a fall in the attraction of electrons from the aldehyde carbonyl group. Thus, in this case the electrophilic properties of the carbonyl group carbon are reduced and the hydration of such a molecule is more difficult than in an acid solution.

This type of change in the state of glyoxylic acid molecules (reduction in the electrophilic properties of the carbonyl group) also affects the reduction potential: Beginning with pH 3.7, in buffer solutions there appears a second wave at more negative potentials (Fig. 2). On the other hand, the appearance of the third wave is also connected with a change in the state of the carbonyl group and also with a corresponding change in the reduction mechanism at very low hydrogen ion concentrations.

Thus, the waves observed correspond to the following reactions:

First wave: 

Second wave: 

Third wave: 

From the schemes presented it is clear that hydrogen ions participate in the electrode reactions corresponding to the first and second waves so that $E_{\frac{1}{2}}$ depends on the pH; with the first wave, $E_{\frac{1}{2}}$ changes by 76 mv per pH unit and with the second wave, by 70 mv.

As Fig. 4 shows, with the third wave there is also a slight change in $E_{\frac{1}{2}}$ with pH (~25 mv per pH unit), which apparently results from a change in the state of the glyoxylic acid molecule with a change in pH. In this case it may be assumed that there is a reaction of the electrophilic carbon atom of the carbonyl group, which bears a certain positive charge, with the negative ions OH^- so that the electrophilicity of this carbon is somewhat reduced with an increase in the OH ion concentration, i.e., with an increase in pH, which also leads to some hindrance to the reduction of the carbonyl group.

In unbuffered (or weakly buffered) solutions, $E_{\frac{1}{2}}$ of the second wave (it evidently corresponded to our third wave) was found to be constant by G. M. Florianovich [2].

We also obtained an analogous result with a base electrolyte of KCl + HCl (or KOH), which was used in the work in [2]. This is most probably explained by the fact that the electrode reaction involving H^+ leads to a sharp change in pH in the layer at the electrode in unbuffered solutions and in actual fact, the whole of the process occurs in an alkaline medium. The absence of a more positive wave, corresponding to the beginning of reduction in an acid medium (as has often been reported in investigation of other substances in unbuffered solutions), is connected with the fact that I in an acid medium is considerably less than I in an alkaline medium and therefore the first and second waves may not actually be noticed with normal heights of the third wave.

The increase in the limiting current, beginning with pH > 6 and appearing especially in the alkaline region, is also connected, on the one hand, with the change in the electrophilic properties of the C = O group, which leads to a fall in the dehydration energy of glyoxylic acid molecules with an increase in pH, and, on the other hand, with the fact that, as in other cases [12-14], OH^- ions catalyze the dehydration of glyoxylic acid molecules.

As these two factors operate simultaneously, the examination of this process is a much more complicated problem than in the case of formaldehyde [10-12] and requires additional investigations.

SUMMARY

1. The polarographic behavior of glyoxylic acid on a mercury dropping electrode was investigated; it was shown that the acid is reduced both in buffered and unbuffered solutions.

2. It was shown that one wave is observed in strongly acid buffer solutions; a second wave appears, beginning with pH 3.5. With a further increase in pH, the height of the first wave falls and the wave disappears completely at pH 5, while the second wave grows. A third wave appears at pH 5.7 with the gradual disappearance of the second (it disappears completely at pH 7.2). The remaining third wave has a $E_{\frac{1}{2}}$ value which changes little with an increase in the pH of the buffer solutions.

3. It was shown that the height of the glyoxylic acid wave depends strongly on pH.

4. It was established that the limiting current obtained during the reduction of glyoxylic acid depends strongly on temperature.

5. From the temperature dependence of the limiting current, we calculated the activation energies of glyoxylic acid dehydration; they decreased from acid to alkaline solutions.

6. It was shown that there is a relation between the state of glyoxylic acid molecules in solution and their polarographic behavior.

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INTERNAL COMPLEX COMPOUNDS AS CONTACT INSECTICIDES

A. P. Terent'ev, E. A. Viktorova, B. M. Esel'son, A. N. Kost, and V. V. Ershov

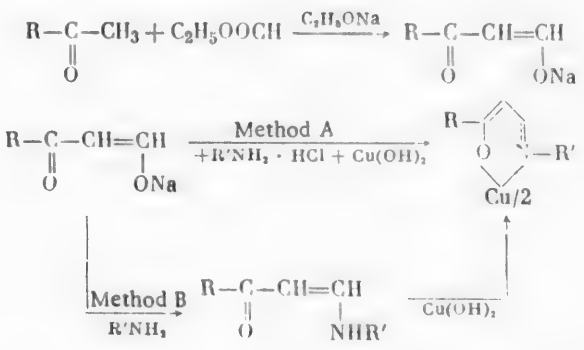
Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2422-2427, July, 1960
Original article submitted May 13, 1959

Until now, internal complex compounds have been studied mainly from the point of view of their possible use for the separation and quantitative determination of cations. However, many data have been accumulated, indicating that many substances among internal complex compounds have a strong physiological action. Thus, copper hydroxyquinolinate is known to be an effective fungicide [1], but in large doses it also harms the plant [2]. In some cases, internal complex compounds behave as bacteriostatic agents (see, for example, [3]). Many cases of physiological activity of internal complex compounds may be found in reviews [4, 5]; however, up to now, no attempts have been made to study this class of compounds as insecticides. This problem is very important as most insects gradually adapt themselves to various poisons so that there is a decrease in the toxicity of the insecticide toward the given form of insect or there appear resistant strains of insects on which the given insecticide has no action.

We started from the hypothesis that metallocyclic compounds, being practically insoluble in water and readily soluble in organic materials, would penetrate readily through the chitin envelope of insects and having entered the organism, would affect the cytochrome (respiratory enzyme), which itself is a metallocyclic compound. Tests of compounds of this class demonstrated the accuracy of our premises. For example, the copper complex of the methylimine of 2-methylheptan-4-on-6-al (MGU-22), which was obtained by formylation of methyl isobutyl ketone with subsequent treatment with methylamine and copper hydroxide, was found to be an effective contact poison against house flies [6].

We undertook the synthesis of copper internal complex compounds from alkylaminomethylene ketones for finding the most effective preparation of this class.



Ketones were first condensed with ethyl formate of methyl formate by Claisen's method. The sodium salts of the hydroxymethylene ketones were dried carefully and used for the subsequent stages without further purifica-

tion. The reaction proceeded best with acetone and methyl ethyl ketone. With an increase in the hydrocarbon chain of the radical, the yields of the corresponding sodium salts fell appreciably (from 80-82 to 50-60%).

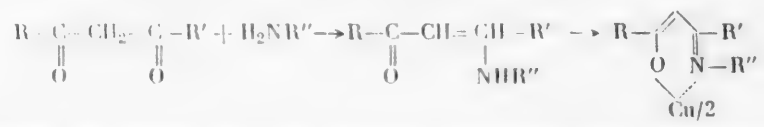
The synthesis of copper complexes of amino ketones from the sodium salts of hydroxymethylene ketones was then achieved by two methods: either directly in one stage from the sodium salt of the hydroxyl ketone by reaction with an amine and copper hydroxide (method A) or with isolation in a pure form of the intermediate alkylaminomethylene ketones, which then reacted with copper hydroxide to form internal complex copper salts (method B).

Method A was simpler and more convenient; however, as many alkylaminomethylene ketones have not been described in the literature, we isolated them in a pure state. In addition, for control and comparison, it was advantageous to prepare the copper derivatives of alkylaminomethylene ketones from the amino ketones themselves. Substances of the same degree of purity were obtained in the two cases (A and B) and the yields of copper complexes (calculated on the sodium salt of the hydroxymethylene ketone) were practically identical (see Table 1).

The alkylaminomethylene ketones were high-boiling, oily, yellow liquids with a sharp, unpleasant odor. When vacuum distilled, methyl- and ethylaminomethyleneacetone decomposed, while the higher alkylaminomethylene ketones distilled without decomposition. The simplest alkylaminomethylene ketones dissolved with difficulty in ether, benzene, and chloroform, but the solubility in organic solvents increased with the higher alkylaminomethylene ketones. All the compounds of this type prepared showed higher alkylaminomethylene ketones. All the compounds of this type prepared showed high exaltation of the molecular refraction (up to 4.5 units), as has already been reported [7].

The copper internal complex compounds of alkylaminomethylene ketones were obtained in yields of 48 to 96%, depending on the structure. In most cases they were black-green, volatile, oily liquids (or more rarely crystals); some of them distilled in vacuum without decomposition; they were readily soluble in all organic solvents and insoluble in water, but on prolonged standing in a moist atmosphere, they were slowly hydrolyzed with the liberation of copper hydroxide. With an increase in the size of the radical at the nitrogen atom the stability of the copper complexes decreased. Table 2 gives the properties* and yields of the compounds of this type prepared.

In addition to copper complexes of alkylaminomethylene ketones obtained from β-keto aldehydes, we synthesized analogous compounds from β-diketones by the same scheme (see Tables 1 and 2).



In these compounds, the introduction of the additional hydrocarbon radical into the molecule of the copper complex sharply reduced the insecticide properties and all the compounds of this type (MGU-67, MGU-68, MGU-86, etc.) showed an insignificant activity against house flies. Preparations of the internal complex type containing copper but no nitrogen were found to be inactive. For example, copper acetylacetonate (MGU-54) had no insecticidal properties. The acetylacetonates of the following other metals were also inactive: sodium (MGU-53), cobalt (MGU-63), nickel (MGU-62). Some activity against house flies was shown by iron acetylacetonate (MGU-43) and another organo-iron compound, ferrocene (MGU-61).

Thus, copper complexes of methylamino- and ethylaminomethylene ketones like MGU-22, 32, 132, and 190 were most interesting as insecticides. The nature of their toxic action differed fundamentally [6] from that of DDT and in accordance with this, the preparation MGU-22, for example, was an effective poison for DDT-resistant flies [8].

EXPERIMENTAL

Synthesis of sodium salts of hydroxymethylene ketones. Into a three-necked flask, fitted with a powerful stirrer, reflux condenser with a calcium chloride tube, and a dropping funnel, were placed 300 ml of absolute ether** and 23 g (1 mole) of finely cut metallic sodium. Then with vigorous stirring and cooling, a mixture of 1

*All the compounds we prepared were tested for insecticidal activity in the Entomology Department of Moscow State University by E. Kh. Zolotarev et al. [6, 8].

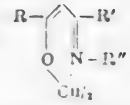
**In the synthesis of the sodium salt of hydroxymethyleneisopropyl acetone, it was necessary to take 800 ml of ether.

TABLE 1. Constants of Alkylaminomethylene Ketones RCOCH = C(R') NHR"

R	R'	R"	Name	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	EM_D	% N found	% N calc.	Yield (%)
CH_3	H	C_2H_5	Ethylaminomethylene-acetone*	85—86° (5)	1.5335	0.9670	36.16	33.64	2.52	11.7	12.3	42
CH_3	H	iso-C_3H_7	Isopropylaminomethy-leneacetone	90 (5)	1.5252	0.9385	41.6	38.26	3.34	11.05	11.0	28
CH_3	H	C_4H_9	Butylaminomethylene-acetone	98 (5)	1.5200	0.9187	46.8	42.88	3.92	10.03	10.0	33
C_2H_5	H	CH_3	Methylaminomethylene-butan-2-one	95—96 (5)	1.5540	0.9858	36.66	33.64	3.02	11.8	12.4	34
C_3H_7	H	CH_3	Methylaminoethylene-pentan-2-one	78 (2)	1.5275	0.9522	41.02	38.26	2.76	10.6	11.0	53
iso-C_4H_9	H	CH_3	Methylaminomethylene-isopropylacetone	96 (8)	1.5280	0.9269	46.81	42.88	3.83	10.0	10.0	70
C_5H_{11}	H	CH_3	Methylaminomethylene-heptan-2-one	109 (8)	1.5195	0.9400	49.6	47.5	2.1	8.80	9.0	65
iso-C_4H_9	H	C_2H_5	Ethylaminomethylene-isopropylacetone	111 (14)	1.5251	0.8923	52.0	47.5	4.5	8.65	9.0	62
iso-C_4H_9	H	iso-C_3H_7	Isopropylaminoethylene-isopropylacetone	111 (13)	1.5088	0.8920	56.0	52.11	3.99	8.0	8.25	58
CH_3	CH_3	CH_3	Methylaminoacetylace-tone	94—95 (15)	1.5220	0.9652	35.53	33.64	1.89	12.5	12.4	93
CH_3	C_2H_5	CH_3	Methylaminopropionyl-acetone	94—95 (5)	1.5250	0.9530	40.61	38.28	2.35	11.0	11.0	94
CH_3	C_4H_9	CH_3	Methylaminoisovaleryl-acetone	108—109 (2)	1.5172	0.9464	50.53	47.50	3.03	8.9	9.0	95
CH_3	C_4H_9	C_2H_5	Ethylaminoisovaleryl-acetone	106—107 (3)	1.5088	0.8900	54.03	52.11	2.42	8.0	8.25	58

* Literature data [7]: b.p. 63—64° (4 mm), n_D^{20} 1.5427, d_4^{20} 0.9543.

TABLE 2. Properties of Copper Derivatives of Alkylaminomethylene Ketones



Number	R	R′	R″	Melting point	% N found	% N calc.	% Cu found	% Cu calc.	Yield (%)	Bulk state	Mortality (%) of flies after a day's contact with the substance (100 mg/m²)
MGU 32	CH_3	H	CH_3	99° *	—	—	—	—	70	Black crystals	100
MGU -190	CH_3	H	C_2H_5	4	9.6	9.7	21.9	22.2	96	Black liquid	100
MGU -171	CH_3	H	iso-C_3H_7	57	8.8	8.85	19.7	20.2	90	Black-green needles	64
MGU -204	CH_3	H	C_4H_9	—	8.5	8.14	—	18.6	87	Viscous oily liquid	**
MGU -172	CH_3	H	C_5H_{11}	—	7.2	7.52	15.4	16.1	75	The same	**
MGU -173	CH_3	H	C_5H_{11}	11	6.9	7.07	15.5	16.0	83	" "	**
MGU -201	C_2H_5	H	CH_3	69	9.6	9.7	19.8	22.2	69	Lustrous black crystals	—
MGU -202	C_3H_7	H	CH_3	48	8.7	8.8	20.0	20.2	92	The same	—
MGU -22	iso-C_4H_9	H	CH_3	27	8.1	8.1	18.3	18.6	65	" "	100
MGU -132	iso-C_4H_9	H	C_2H_5	—	7.53	7.52	—	17.2	77	Black liquid	100
MGU -175	iso-C_4H_9	H	C_3H_7	—	7.0	7.0	—	16.0	72	The same	39
MGU -174	iso-C_4H_9	H	C_4H_9	9	6.7	6.54	14.2	14.8	70	" "	28
MGU -176	iso-C_4H_9	H	C_5H_{11}	—	6.0	6.14	—	13.9	74	" "	6
MGU -177	iso-C_4H_9	H	C_5H_5	—	5.4	5.85	13.2	13.3	63	" "	19
MGU -181	$(CH_3)_2C{=}CH$	H	CH_3	18	8.5	8.23	18.8	18.6	48	Black crystals	92
MGU -182	$(CH_3)_2C{=}CH$	H	C_2H_5	—	8.2	7.89	17.0	17.3	52	Black liquid	91
MGU -184	$(CH_3)_2C{=}CH$	H	C_4H_9	—	5.8	6.60	15.2	14.9	57	The same	12
MGU -203	C_5H_{11}	H	CH_3	19	7.6	7.5	16.8	17.2	92	" "	—
MGU -57	$(CH_3)_3C$	H	CH_3	93	7.85	8.14	18.3	18.6	70	Lustrous black crystals	12
MGU -108	CH_3	CH_3	CH_3	90	9.6	9.7	21.8	22.2	93	The same	24 ***
—	C_2H_5	CH_3	CH_3	55	8.85	8.55	19.6	20.2	55	" "	—
—	iso-C_4H_9	CH_3	CH_3	65	—	7.5	16.7	17.2	86	Black crystals	—
—	iso-C_4H_9	CH_3	C_2H_5	56	6.65	7.0	16.0	16.0	60	The same	—
MGU -86	CH_3	CH_3	C_6H_5	48	6.4	6.8	15.3	15.5	62	" "	15

* Literature data [9]: m.p. 99-100°.

** Substance readily destroyed in moist air.

*** Data for a concentration of 250 mg/m².

mole of ethyl formate and 1 mole of ketone in 100 ml of ether was added in small portions. The reaction mass evolved heat and gradually deposited a yellow precipitate. The rate of addition of the mixture was adjusted so that the ether boiled gently. After 1-2 hr, the reaction mixture thickened and then the precipitate was collected by filtration, washed with ether, and dried in air to remove ether and then in a vacuum desiccator over sulfuric acid.

Preparation of alkylaminomethylene ketones from β-diketones. Into a round-bottomed flask, fitted with a reflux condenser and a tube passing to the bottom of the flask, was placed 1 mole of diketone and dry, gaseous methylamine (1 mole) slowly passed into the flask. With higher-molecular amines, the latter were cooled and added dropwise to the diketone (the reaction flask was immersed in a cooling mixture). The alkylaminomethylene ketone formed was separated from the aqueous layer, dried with potassium carbonate, and vacuum distilled.

Preparation of alkylaminomethylene ketones from sodium salts of hydroxymethylene ketones. In a thick-walled, round-bottomed flask were placed 1 mole of sodium salt of hydroxymethylene ketone, 1 mole of baked sodium sulfate, and 1 mole of alkylamine hydrochloride. The flask was closed and shaken vigorously for some time and then the dry mass liquified. In the reaction of the sodium salt of hydroxymethyleneacetone with alkylamine hydrochlorides, the mixture became liquid after 20-30 min and in the preparation of the other alkylaminomethylene ketones, only after 2-3 hr of vigorous shaking. The liquid reaction mass was left for 2 hr at room temperature and then a reflux condenser connected and the mixture heated on a water bath for 30-40 min. The alkylaminomethylene ketone formed was filtered free from inorganic salts and the precipitate carefully pressed out and washed with ether or acetone. The acetone solution was added to the filtrate and the mixture dried with potassium carbonate; after removal of the solvent, the residue was vacuum distilled. Redistillation yielded pure aminomethylene ketones, whose constants are given in Table 1.

Preparation of copper derivatives of alkylaminomethylene ketones. Into a round-bottomed flask, fitted with a stirrer and reflux condenser, were placed 1 mole of alkylaminomethylene ketone and 0.6 mole of freshly prepared copper hydroxide and the reaction mixture stirred vigorously. After 30-40 min, the mixture itself evolved heat and became homogeneous; when the spontaneous evolution of heat ceased, the mixture was heated on a water bath for 1 hr and then left overnight. The reaction product was extracted with ether, the ether dried with potassium carbonate, the ether removed, and the residue recrystallized from acetone.

Preparation of copper derivatives of methylaminomethylene ketones from sodium salts of hydroxymethylene ketones [9]. Into a thick-walled, round-bottomed flask were placed 1 mole of the dry sodium salt of the hydroxymethylene ketone, 1.05 mole of alkylamine hydrochloride, and 0.55 mole of copper hydroxide. The flask was carefully closed and the mixture shaken vigorously, when it gradually evolved heat, became liquid, and then solidified as a homogeneous mass. The subsequent treatment was as described above. Table 2 gives the properties and yields of the copper derivatives of aminomethylene ketones. The nitrogen in the compounds synthesized was determined by the Kjeldahl method. The copper was determined in the following way: The internal complex compounds of copper were decomposed with acetic acid, the copper precipitated as the hydroxyquinolinate, and the metal determined either volumetrically or gravimetrically. Titration was difficult without precipitation of the hydroxyquinolinate.

SUMMARY

1. The synthesis of a new class of contact insecticides, which are internal complex compounds, is described.

2. Internal copper complex compounds of alkylaminomethylene ketones are most effective.

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REACTION OF 8-CAFFEINEALDEHYDE WITH DIALKYLPHOSPHOROUS ACIDS

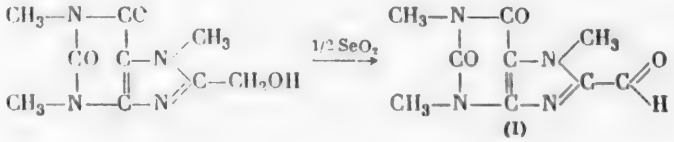
B. P. Lugovkin

All-Union Scientific Research Institute for the Protection of Labor of the All-Union Central Council of Trade-Unions, Kazan'

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2427-2429, July, 1960
Original article submitted June 29, 1959

E. S. Golovchinskaya described the synthesis and chemical properties of 8-caffeinealdehyde [1]. She obtained it in 54% yield by hydrolysis of 8-dichloromethylcaffeine.

We synthesized 8-caffeinealdehyde (I) by oxidation of 8-hydroxymethylcaffeine with selenium dioxide by heating the components to 145-160°. The aldehyde yield was 80%.



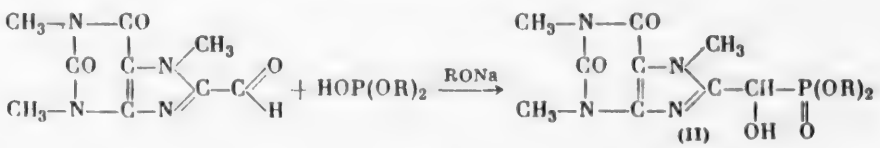
(I)

When heated with selenium dioxide under the same conditions (150-160°), 8-caffeinealdehyde changed little; heating to 225° yielded a complex mixture from which it was impossible to isolate 8-caffeinecarboxylic acid.

An attempt to prepare 8-caffeinealdehyde from 8-methylcaffeine was unsuccessful. The oxidation of 8-methylcaffeine by selenium dioxide was accompanied by considerable evolution of heat (the temperature rose from 116 to 225°). It was possible to extract 8-caffeinealdehyde from the reaction products in only a very small amount (3.4%). The aldehyde was identified as the Schiff's base (anil) [1].

Continuing previous work on the synthesis of esters of 8-methylcaffeinephosphinic acid [2] (obtained by the Arbuzov reaction with 8-chloromethylcaffeine and trialkylphosphites), we investigated the condensation of 8-caffeinealdehyde with dialkylphosphorous acids.

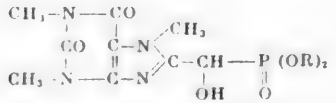
By the reaction of V. S. Abramov [3], we were able to prepare the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, and diisobutyl esters of α-hydroxy-8-methylcaffeinephosphinic acid (II).



(II)

Condensation occurred when alcohol solutions of the sodium alcoholates were added and was accompanied by the evolution of heat. In most experiments, the reaction was completed by heating to 95°. The esters obtained were colorless, crystalline substances. With an increase in the molecular weight of the ester radical of the phosphinic acid, crystallization of the esters became more difficult. Their solubility in water also fell in the same series.

Reaction of 8-Caffeinealdehyde with Dialkylphosphorous Acids and Characteristics of the α-Hydroxy-8-methylcaffeine-phosphinic Esters



R	Amounts of reagents (g)		Catalyst	Rise in temperature during reaction (from-to)	Formula of ester	Ester yield (%)	Melting point	% P	
	dialkyl-phosphorous acid	8-caffeine-aldehyde						calculated	found
CH_3	0.55	1.0	CH_3ONa	25 – 95°	$C_{11}H_{17}O_6N_4P$	75.8	132 – 132.5°	9.33	9.02
C_2H_5	0.50	0.70	C_2H_5ONa	20 – 60	$C_{13}H_{21}O_6N_4P$	44.2	80 – 80.5	8.60	8.54
n-C_3H_7	0.60	0.70	C_3H_7ONa	22 – 50	$C_{15}H_{25}O_6N_4P$	87.7	77 – 77.5	7.98	7.93
iso-C_3H_7	0.64	0.75	CH_3ONa	21 – 40	$C_{15}H_{25}O_6N_4P$	68.7	144 – 145	7.98	8.51
n C_4H_9	0.75	0.70	C_4H_9ONa	21 – 40	$C_{17}H_{29}O_6N_4P$	45.8	54 – 55	7.44	7.38
iso-C_4H_9	0.70	0.70	CH_3ONa	23 – 87	$C_{17}H_{29}O_6N_4P$	32.0	106 – 107	7.44	7.43

The yields of the diethyl, dibutyl, and diisobutyl esters were lower than those of the other esters due to the formation of by-products.

The results of investigating the reactions of 8-caffeinealdehyde with dialkylphosphorous acids and the characteristics of the esters of α-hydroxy-8-methylcaffeinephosphinic acid synthesized are given in the table.

EXPERIMENTAL

8-Caffeinealdehyde. A carefully ground mixture of 8.75 g of 8-hydroxymethylcaffeine• (m.p. 224°) and 2.6 g of selenium dioxide was heated in an Erlenmeyer flask on a metal bath (Wood's alloy). The oxidation began at 95° (thermometer in reaction mixture) with a sharp rise in temperature to 145°. For completion of the reaction the mixture was heated to 160° for 5 min. The solid product was dissolved in hot chloroform and separated from the black selenium (1.4 g). The solution was heated with activated charcoal; washing the charcoal three times with hot chloroform and removal of the solvent yielded 7.0 g of aldehyde as light yellow crystals with m.p. 164-165°. After a second heating with charcoal, the product formed almost colorless crystals with m.p. 166°. A mixed melting point with authentic aldehyde• was not depressed (m.p. 166-167°).

Esters of α-hydroxy-8-methylcaffeinephosphinic acid. To a mixture of 8-caffeinealdehyde and dialkylphosphorous acid was added 0.1-0.2 ml of a saturated alcohol solution of sodium alcoholate. The reaction was carried out with careful stirring (with the thermometer in a closed tube) of the mixture and was accompanied by a rise in temperature. For completion of the reaction, the mixture was carefully heated to 95°. The reaction products were thick liquids, which crystallized rapidly in the case of the methyl and ethyl esters; the other esters crystallized after standing for various times.

The methyl, ethyl, and diisobutyl esters were recrystallized from the amorphous by-products of the reaction by precipitation of them from toluene solution with dry ether; they crystallized after evaporation of the diethyl ether. The dipropyl and diisopropyl esters were heated with active charcoal in chloroform solution and were recrystallized after evaporation of the solvent. The esters were recrystallized from light ligroin for analysis.

The methyl, ethyl, and diisopropyl esters dissolved in cold water and the other esters dissolved in water on heating; they dissolved in alcohol, ether, chloroform, and toluene and with difficulty in light ligroin.

SUMMARY

1. 8-Caffeinealdehyde was obtained in almost quantitative yield by oxidation of 8-hydroxymethylcaffeine with selenium dioxide.

2. The reaction of 8-caffeine aldehyde with dialkylphosphorous acids in the presence of sodium alcoholates as catalysts was studied. Esters of α-hydroxy-8-methylcaffeinephosphinic acid were synthesized.

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• We would like to thank E. S. Golovchinskaya for providing caffeine derivatives.

•• Original Russian pagination. See C. B. translation.

ORDER OF ADDITION OF WATER AND ALCOHOLS TO VINYLACETYLENES

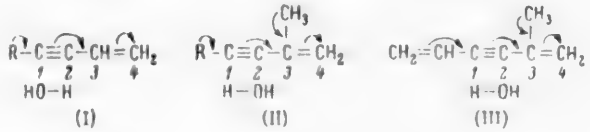
A. A. Petrov and B. S. Kupin

Lensovet Leningrad Technological Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2430, July, 1960
Original article submitted March 9, 1960

The order of addition of water under the conditions of the Kucherov reaction and of alcohols in the presence of KOH to vinylalkylacetylenes (I) is the same and agrees well with the theory of electron displacements [1]. At the same time, the addition of water to isopropenylalkylacetylenes (II) [2] and also to vinylisopropenylacetylene (III) [3] is not in accordance with the polarization which might have been assumed for these hydrocarbons.

The anomalous addition of water to (II) and (III) may be explained by steric hindrance in the formation of the intermediate mercury complex if it is assumed that the reaction has an electrophilic character in the first stage (the radical at C_3 interferes with the approach of mercury to C_2).



(I) (II) (III)

For confirmation of this hypothesis, it was necessary to show that the order of addition of nucleophilic reagents in the absence of heavy metal catalysts, for example, the addition of methanol in the presence of KOH, corresponds to the general rule.

As a result of experiments on the addition of methanol to isopropenylmethylacetylene in the presence of KOH, we obtained a diene enol ether with b.p. 67–72° (100 mm), d_4^{20} 0.8442, n_D^{20} 1.4580.

Found %: C 74.25, 74.13; H 10.35, 10.72. $C_7H_{12}O$. Calculated %: C 75.00; H 10.71.

Infrared spectrum: 793 (s), 875 (s), 955 (med), 980 (w), 1080 (s), 1149 (med), 1175 (s), 1202 (s), 1257 (s), 1315 (s), 1336 (s), 1377 (s), 1388 (s), 1448(s), 1463(s), 1575(s), 1620(s), 1654(s), 1689(med), cm^{-1}.

Hydrolytic cleavage of the ether with dilute sulfuric acid yielded mesityl oxide, which did not contain any ethyl isopropenyl ketone.

B. p. 128–131°, d_4^{20} 0.8597, n_D^{20} 1.4398.

Infrared spectrum: 820 (med), 897 (med), 965 (s), 1017 (med), 1070 (med), 1165 (s), 1218 (s), 1261 (med), 1357 (s), 1376 (s), 1446 (s), 1620 (s), 1692 (s), cm^{-1}.

The 2,4-dinitrophenylhydrazone had m.p. 200° (from alcohol).

Hydrogenation of the mesityl oxide obtained over $Pd/CaCO_3$ yielded methyl isobutyl ketone, which was identical with authentic methyl isobutyl ketone as regards constants, infrared spectrum and melting point of 2,4-dinitrophenylhydrazone. Thus, it was established that the order of nucleophilic addition of alcohol to isopropenylmethylacetylene differs from the order of addition of water under the conditions of the Kucherov reaction, which confirms the above hypothesis on the mechanism of this reaction and the reasons for the anomalous addition of water to (II) and (III).

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*Original Russian pagination. See C. B. translation.

POLYMERIZATION OF SUBSTITUTED DIVINYL KETONES WITH THE FORMATION OF RINGS

S. G. Matsoyan and M. G. Avetyan

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR

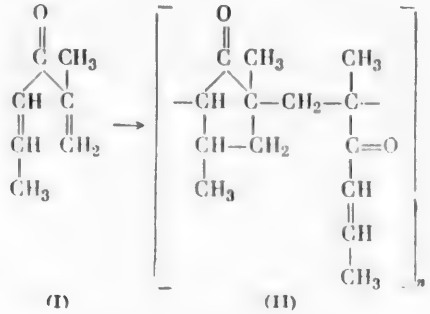
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2431-2432, July, 1960
Original article submitted March 15, 1960

A new form of polymerization was discovered recently and this consists of intramolecular ring closure of isolated dienes [1] with the simultaneous intermolecular growth of the chain. It seemed interesting to study the possibility of such cyclic polymerization of substituted divinyl ketones. The synthesis and various conversions of these dienones, especially to cyclopentenones, have been the subject of many investigations by I. N. Nazarov et al. [2].

By polymerization of 2-methyl-1,4-hexadien-3-one (I) in the presence of 1 mol. % of benzoyl peroxide, we obtained a white powdery polymer (m.p. 145-150°) (II), which dissolved readily in organic solvents.

Found %: C 76.26, 76.00; H 9.29, 9.50. $(C_7H_{10}O)_n$. Calculated %: C 76.32; H 9.14.

The characteristic viscosity in benzene equalled 0.11. Ozonization and bromination of polymer (II) indicated about 25% of unsaturation, calculated on two double bonds in the monomer (100%). Hydrolysis of the polymer ozonide (m.p. 165-170° with decomp.) formed acetic acid (formic acid was not detected by the calomel method) and a polyacid, which was partly soluble in water. Titration of the polyacid with 0.5 N alkali solution also showed that the polymer unit was formed from two molecules of monomer (I). Apparently, there was simultaneous cyclopolymerization of one molecule and vinyl polymerization of a second molecule of monomer (I) at the isopropenyl group.



(I) (II)

This polymerization mechanism is evidently explained by steric difficulties in the direct formation of a polymer chain by cyclopentane rings.

The infrared spectrum of polymer (II) contained an intense band of the carbonyl group of the cyclopentane ring (1737 cm^{-1}) and also the frequencies of a conjugated double bond (1624 cm^{-1}) and a carbonyl group (1690 cm^{-1}). By comparing the infrared spectra of monomer (I) and polymer (II), we determined the degree of unsaturation, which was almost exactly a factor of 4 less (25%) in polymer (II).

2,5-Dimethyl-1,4-hexadien-3-one was polymerized analogously. The polymerization of substituted divinyl ketones is being studied.

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*Original Russian pagination. See C. B. translation.

N-DI-(CHLOROETHYL)-AMIDES OF AMINO CARBOXYLIC ACIDS AND THEIR PEPTIDES

I. METHOD OF PREPARING N-DI-(CHLOROETHYL)-AMIDE OF GLYCINE AND RELATED COMPOUNDS

T. S. Safonova and S. I. Sergievskaya

S. Ordzhonikidze All-Union Chemicopharmaceutical Scientific Research Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2432-2433,
July, 1960
Original article submitted March 24, 1960

Compounds of the type $RN(CH_2CH_2Cl)_2$, where R represents various radicals (aliphatic, aromatic, aliphatic-aromatic, etc.) are widely known and have been synthesized in large numbers. However, little attention has been paid to the acylation of N-di-(chloroethyl)-amides and published artlicles have been limited to the synthesis and investigation of N-di-(chloroethyl)-amides of some aliphatic and aromatic acids [1].

In connection with our previous work [2], we undertook the synthesis of a series of N di-(chloroethyl)-amides of aliphatic amino acids and their peptides to study their biological action. We began with work on the simplest representatives of this class. In the search for a method of preparing these compounds, we tried various methods of protecting the amino group in the acids and aminolyzing the carboxyl group. The following preparation method was developed: first, either esters of N-tritylglycine, $(C_6H_5)_3C-NH-CH_2COOR$ (methyl, ethyl, and nitrophenyl), or the acid chloride of N-phthalylglycine were treated with diethanolamine to give the corresponding N-di-(hydroxyethyl)-amide and then the trityl (with 75% acetic acid) or phthalyl (with hydrazine hydrate) group was removed. The final stage consisted of the action of thionyl chloride on the N-di-(hydroxyethyl)-amide hydrochlorides. We obtained the N-di-(hydroxyethyl)-amides of the following amino acid derivatives: N-trityl-glycine, N-trityl-α-alanine, N-phthalylglycine, N-phthalyl-α-alanine, and N-phthalyl-β-alanine. We determined the infrared absorption spectra of all the compounds given and they contained an absorption band, characteristic of the amide bond.

The action of thionyl chloride on the N-di-(hydroxyethyl)-amide of glycine hydrochloride yielded the hydrochloride of the corresponding N-di-(chloroethyl)-amide.

N-Tritylglycine N'-di-(hydroxyethyl)-amide had m.p. 127-128°; it was soluble in alcohol, difficultly soluble in benzene, and insoluble in water. The infrared spectrum contained the absorption band of an amide bond (1623 cm^{-1}).

Found %: C 74.08; H 7.02; N 7.05. $C_{25}H_{28}O_3N_2$. Calculated %: C 74.23; H 6.97; N 6.92.

N-Phthalylglycine N'-di-(hydroxethyl)-amide had m.p. 156-158°; it was soluble in alcohol and water. The infrared spectrum had the absorption band of an amide bond (1629 cm^{-1}).

Found %: C 57.37; H 5.47; N 9.38. $C_{14}H_{16}O_5N_2$. Calculated %: C 57.52; H 5.51; N 9.58.

Glycine-N-di-(chloroethyl)-amide hydrochloride had m.p. 154-155° (decomp.); it was soluble in water and alcohol.

Found %: C 30.25; H 5.36; N 11.95; Cl 44.88. $C_6H_{12}ON_2Cl_2 \cdot HCl$. Calculated %: C 30.59; H 5.56; N 11.85; Cl 45.15.

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*Original Russian pagination. See C. B. translation.

SIMILARITY IN CHEMICAL STRUCTURE AND BIOLOGICAL ACTIVITY OF RIBONUCLEASE AND INCREPAN

S. V. Andreev, R. P. Evstigneeva, A. M. Mirzabekov, N. P. Speranskaya, and N. A. Preobrazhenskii

Moscow Institute of Fine Chemical Technology and Institute of Pharmacology and Chemotherapy, Academy of Medical Sciences of the USSR
Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, p. 2433, July, 1960
Original article submitted April 27, 1960

The preparation increpan, which is isolated from the pancreas of cattle [1], has a prolonged hypotensive action when administered to animals intravenously or perorally [2, 3]. Increpan also lowers the arterial pressure in hypertonic patients.

The protein fraction obtained from increpan after removal of the nucleic acids by the method of Spirin and Belozerskii was found to be identical with ribonuclease in amino acid composition (determined by a combined method of paper electrophoresis and chromatography) and infrared and ultraviolet spectra.

In this connection, the biological activity of ribonuclease in this direction was tested. In preliminary experiments on acute cases in cats, ribonuclease was found to have a more intense hypotensive action than increpan and its protein fraction. It may be conjectured that ribonuclease is an important biochemical factor controlling the level of the arterial pressure in man and animals.

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SYNTHESIS OF N-(D β-TETRAACETYLGLUCOPYRANOSYL)-INDOLE

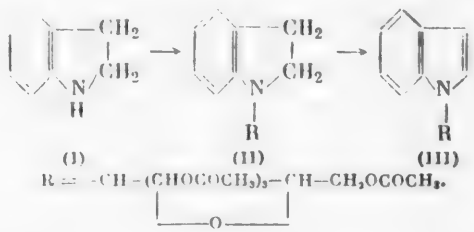
N. N. Suvorov and M. N. Preobrazhenskaya

S. Ordzhonikidze All-Union Chemicopharmaceutical Scientific Research Institute

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2434-2435,
July, 1960
Original article submitted May 3, 1960

Indole derivatives play a substantial role in the pathogenesis of leucoses [1]. In this connection, the preparation of various indolyl glucosides and the study of their biological activity are of great interest.

We prepared N-(D-β-tetraacetylglucopyranosyl)-indole (III) according to the following scheme:



Reaction of indoline (I) with glucose and subsequent acetylation with acetic anhydride in pyridine formed N-(D-β-tetraacetylglucopyranosyl)-indoline (II) in 60% yield.

M.p. 117.8-118.5° (from alcohol). $[\alpha]_D^{20}$+11.7° (C_6H_6, c 6); $[\alpha]_D^{20}$+11.3° ($CHCl_3$, c 6). Ultraviolet spectrum (in alcohol): λ_{max} 242 mμ (lg ε 4.07); λ_{max} 295 mμ (lg ε 3.32) Rf 0.04 (n-heptane–β-phenoxyethanol).

Found %: C 59.12; H 6.25; N 3.35; CH_3CO 38.2. $C_{22}H_{27}O_9N$. Calculated %: C 58.79; H 6.05; N 3.12; CH_3CO 38.3.

Substance (II) was also obtained by the reaction of indoline (I) with α-tetraacetylglucopyranosyl bromide, with α-pentaacetylglucopyranose, and with β-pentaacetylglucopyranose (60-90% yield). The generally adopted mechanism of nucleophilic substitution in carbohydrates makes it possible to assign a β configuration to compound (II) [2]. Hydrolysis of compound (II) with 5% acetic acid led to indoline (I) and 2,3,4,6-tetraacetylglucopyranose, which was isolated as α-pentaacetylglucopyranose.

Dehydrogenation of compound (II) with chloranil [3] (heating 0.01 mole of substance (II), 0.01 mole of chloranil, and 40 ml of anhydrous xylene for 6 hr) gave N-(D-β-tetraacetylglucopyranosyl)-indole (III). The yield of pure substance was 20-25%.

M.p. 148.5-149.5° (from alcohol); 158.5-159° (from ligroin). When heated, the form with m.p. 148.5-149.5° changed to the form with m.p. 158.5-159°. The infrared spectra of the two forms (solid substances in vaseline oil) were the same.

Ultraviolet spectrum: λ_{max} 288 mμ (lg ε 3.48); λ_{max} 264 mμ (lg ε 3.38); λ_{max} 222 mμ (lg ε 4.46). $[\alpha]_D^{20}$ − 18.6°. (C_6H_6, 3.5); $[\alpha]_D^{20}$ −1.7 ($CHCl_3$, c 6).

Found %: C 59.05; H 5.86; N 3.05; CH_3CO 38.1. $C_{20}H_{25}O_9N$. Calculated %: C 57.75; H 5.63; N 2.13; CH_3CO 38.3.

Ehrlich's reagent gave a yellow color with compound (II) and a red color with compound (III). The deactylation of substance (III) and the properties and also phosphorylation of N-(D-glucosyl)-indole are being studied.

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*Original Russian pagination. See C. B. translation.

CYCLOPROPYLMESITYLENE AND p-CYCLOPROPYLCUMENE

R. Ya. Levina, V. N. Kostin, P. A. Gembitskii, S. M. Shostakovskii, and E. G. Treshchova

Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2435-2436, July, 1960
Original article submitted May 11, 1960

It is known [1,2] that conjugation of the three-membered carbon ring with the benzene ring in the molecule of cyclopropylbenzene (phenylcyclopropane) causes an increase in the intensity of some of the lines characteristic of the benzene ring in the Raman spectrum in comparison with the spectra of benzene and alkylbenzenes.

In the present work, we synthesized and studied the physical properties, including the Raman spectra, of p-cyclopropylcumene and cyclopropylmesitylene (they have not been described in the literature).

The presence of the isopropyl group in the position para to the three-membered ring in the molecule of p-cyclopropylcumene leads to an increase in the electron density in the benzene ring and hence an increase in its conjugation with the three-membered ring, which is reflected in the Raman spectrum of this hydrocarbon. We observed this phenomenon previously in studying the Raman spectrum of p-cyclopropyltoluene [1,3].

In the cyclopropylmesitylene molecule, the two methyl groups ortho to the three-membered ring create steric hindrance [4] so that the cyclopropyl group cannot occupy a position favorable to conjugation.

The experimental data obtained confirmed what has been stated: The intensity of the line at ~1600 cm^{-1} (line of the asymmetric valence vibration of the benzene ring C = C bond) in the spectrum of cyclopropylmesitylene was close to the value in the spectrum of mesitylene itself, while the intensities of this line in the spectra of cyclopropylbenzene, cyclopropyltoluene, and cyclopropylcumene were considerably higher than in the spectra of benzene, toluene, and cumene, respectively (see table).

Thus, judging by the frequency ~1600 cm^{-1} (the intensity of this is affected most strongly by conjugation of the benzene ring with the three-membered ring [1,3,5]), there is practically no conjugation in cyclopropylmesitylene.

p-Cyclopropylcumene (obtained by catalytic decomposition of the corresponding pyrazoline) had the following constants after distillation on a column (40 theoretical plates):

b.p. 90° (5 mm), $n^{20}D$ 1.5180, d_4^{20} 0.9158, MR_D 52.89. $C_{12}H_{16}F_3\Delta$. Calculated 52.52. $\Delta\nu$: 390 (122), 460 (60), 642 (213), 769 (583), 793-833 (356), 895 (710), 958 (100), 1020 (358), 1042-1056 (350), 1104 (180), 1190 (300), 1222 (900), 1308 (285), 1364 (545), 1434-1460 (512), 1613 (1585) cm^{-1}.

Cyclopropylmesitylene was synthesized by two methods: catalytic decomposition of 3-p-mesitylenepyrazoline and methylenation [6] of vinylmesitylene. After the usual treatment and distillation on a column (80 theoretical plates), the two cyclopropylmesitylene preparations had the same constants:

b.p. 103° (9 mm), 97° (6 mm), n_D^{20} 1.5250, d_4^{20} 0.9315, MR_D 52.70. $C_{12}H_{16}F_3\Delta$. Calculated 52.52. $\Delta\nu$: 238 (292), 382 (200), 474 (112 double), 516 (130 broad), 567–576 (860 double), 674 (107), 901 (260), 958 (215), 1056 (150 broad), 1181 (160), 1219–1241 (170), 1296–1320 (350), 1355 (350), 1379 (560), 1427 (260), 1460–1490 (325), 1612 (532) cm^{-1}.

Line Intensities in the Region of ~1600 cm^{-1} in the Spectra of Benzenes and Cyclopropylbenzenes

Ar-H	I_∞	Ar—◁	I_∞
Benzene	215	Cyclopropylbenzene	920
Toluene	303	p-Cyclopropyltoluene	1200
Cumene	490	p-Cyclopropylcumene	1585
Mesitylene	470	Cyclopropylmesitylene	532

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DISCUSSION

PHYSICOCHEMICAL INVESTIGATION OF THE BINARY SYSTEM HYDRAZINE – ACETIC ACID

V. I. Semishin

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2436-2437, July, 1960
Original article submitted June 1, 1960

An article by I. M. Bokhovkin, entitled "Physicochemical Investigation of the Binary System Hydrazine–Acetic Acid" was published recently in the Journal of General Chemistry [1]. On p. 1793, the author wrote: "There are comparatively few data in the literature on the physicochemical analysis of binary salts formed by hydrazine and organic acids," quoting Vol. 6 of the Technical Reference Encyclopedia [in Russian], published in 1931. On p. 1794, it was stated that "the literature contains no data on the melting point of the system hydrazine–acetic acid."

I. M. Bokhovkin was "unable to investigate the fusion of this system due to the low freezing points of the solutions" and he studied the density, viscosity, surface tension, and specific electrical conductivity of this system.

It should be pointed out, first of all, that I. M. Bokhovkin was apparently unaware of my six published communications on the physicochemical investigation of 15 binary systems of hydrazine with various organic components (Zhur. Obshchei Khim., 1938-1944). He was unfamiliar with the monograph of Audrieth and Ogg, "The Chemistry of Hydrazine" (Russian translation, IL, Moscow, 1954), in which, in addition to references to my work, there are many references to work of foreign scientists.

I was the first to study the acetic acid–hydrazine system by thermal analysis and the results were published [2]. I was also the first to study the specific gravity and viscosity of this system [3].

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SYNTHESIS OF 2,3,6-TRIMETHYLOCTA-2,7-DIEN-6-OL–3-METHYLLINALOOL

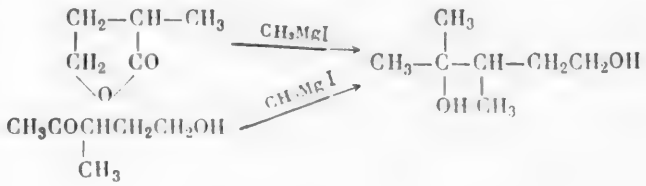
F. N. Stepanov

Translated from Zhurnal Obshchei Khimii, Vol. 30, No. 7, pp. 2437,
July, 1960
Original article submitted February 18, 1960

The authors of [1] stated that they were able to prepare 3-methylpentan-4-on-1-ol by condensation of α-methylacetoacetic ester with ethylene oxide in an alcohol solution of sodium ethylate.

Considerably earlier, it was shown in our laboratory that the condensation of α-methylacetoacetic ester with ethylene oxide yields α-methylbutyrolactone [2]. It was later reported that 3-methylpentan-4-on-1-ol may be obtained from α-acetobutyrolactone by another method [3].

The authors of the article cited [1] were only able to obtain 3-methyllinalool as the final product because the reaction of α-methylbutyrolactone with methylmagnesium iodide evidently led (see scheme) to the same 2,3-dimethylpentan-2,5-diol, which the authors were supposed to have obtained from 3-methylpentan-4-on-1-ol.



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*Original Russian pagination. See C. B. translation.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.